AIR TOXICS EXPOSURE ASSESSMENT WORKSHOP

SESSION II: MONITORING METHODS AND NETWORK DESIGN

Sponsored by:

U.S. EPA

at

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San Francisco, California

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Air Toxics Monitoring Network Development presented by:

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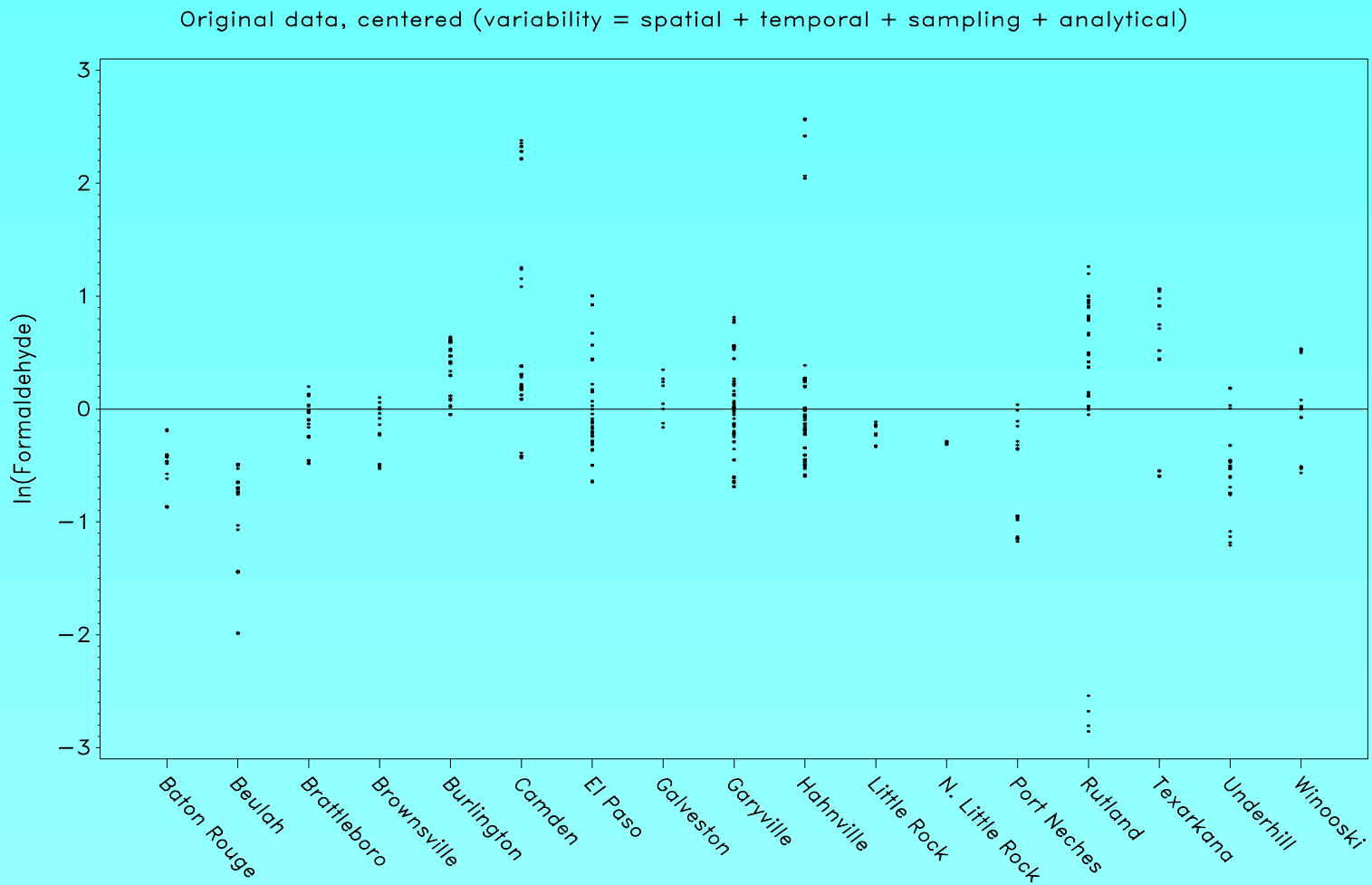
Acknowledgments

- EPA/OAQPS
- STAPPA/ALAPCO
- LADCO
- Air Toxics Monitoring Steering Committee
- ICF/SAI
- State and Local Monitoring Agencies

Sources of Variability in Ambient Air Toxics Monitoring Data

UATMP Data

- 24-hour time integrated measurements of VOCs and carbonyls
  - VOCs measured according to Compendium Method TO-15
  - carbonyls measured according to Method TO-11A
- Duplicate and replicate samples spanning the years 1996-1999
  - i.e., multiple sites, multiple days within sites, duplicate samples on each day at each site, and replicate analyses of each collected sample
- Allows for apportionment and quantification of different sources of variability



Variability = spatial + temporal + sampling + analytical

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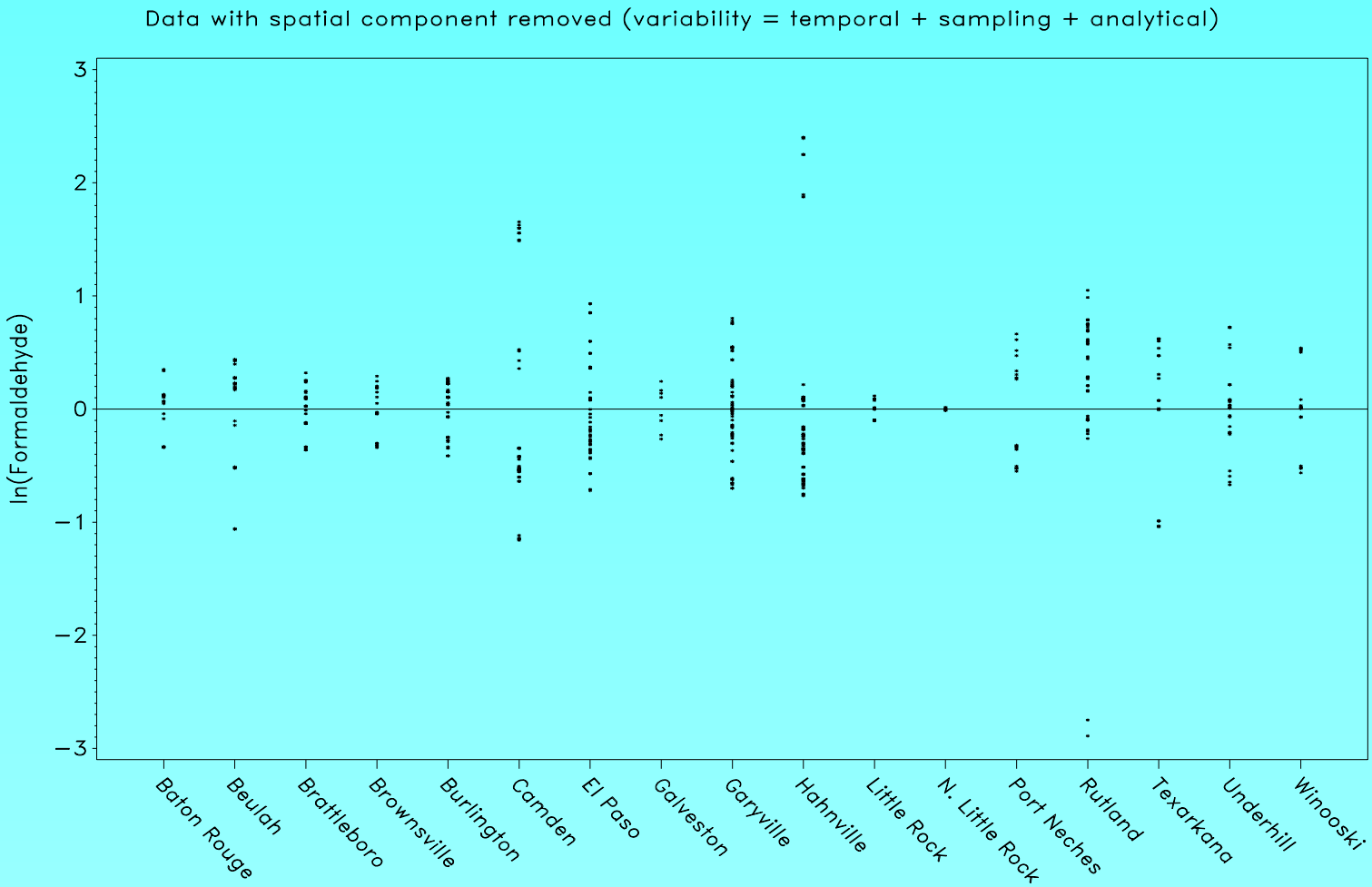

Variability = temporal + sampling + analytical

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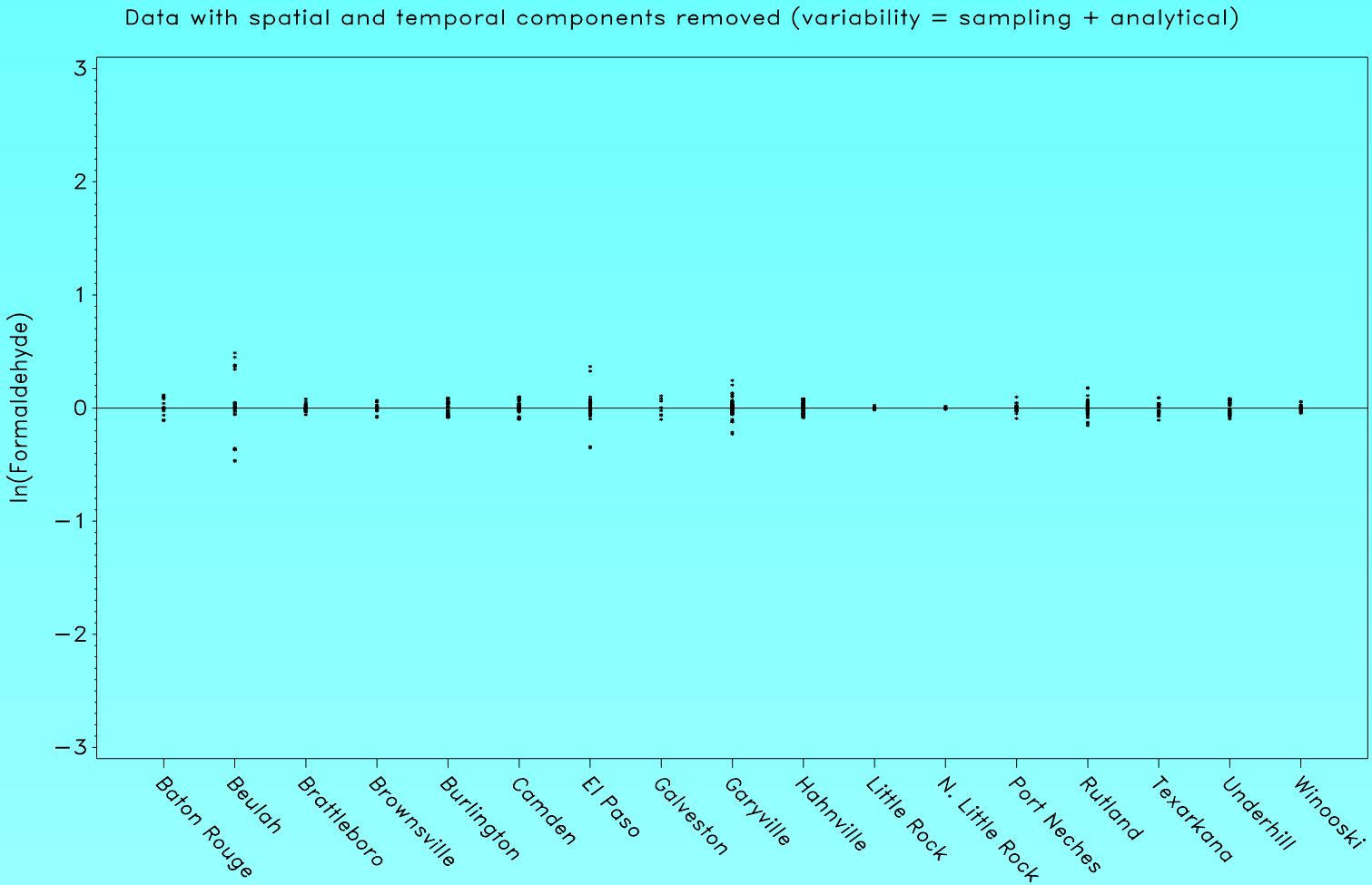

Variability = sampling + analytical

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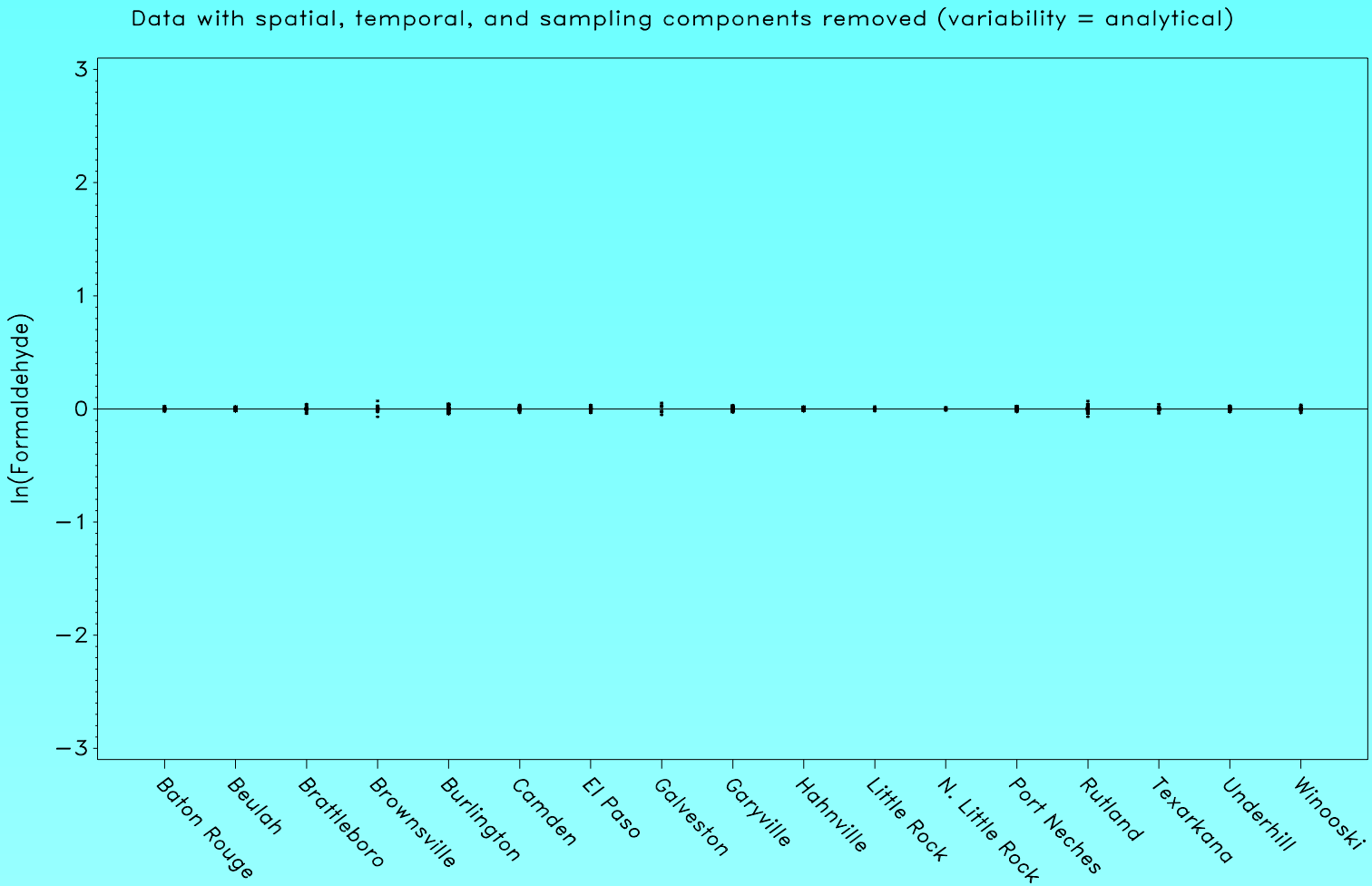
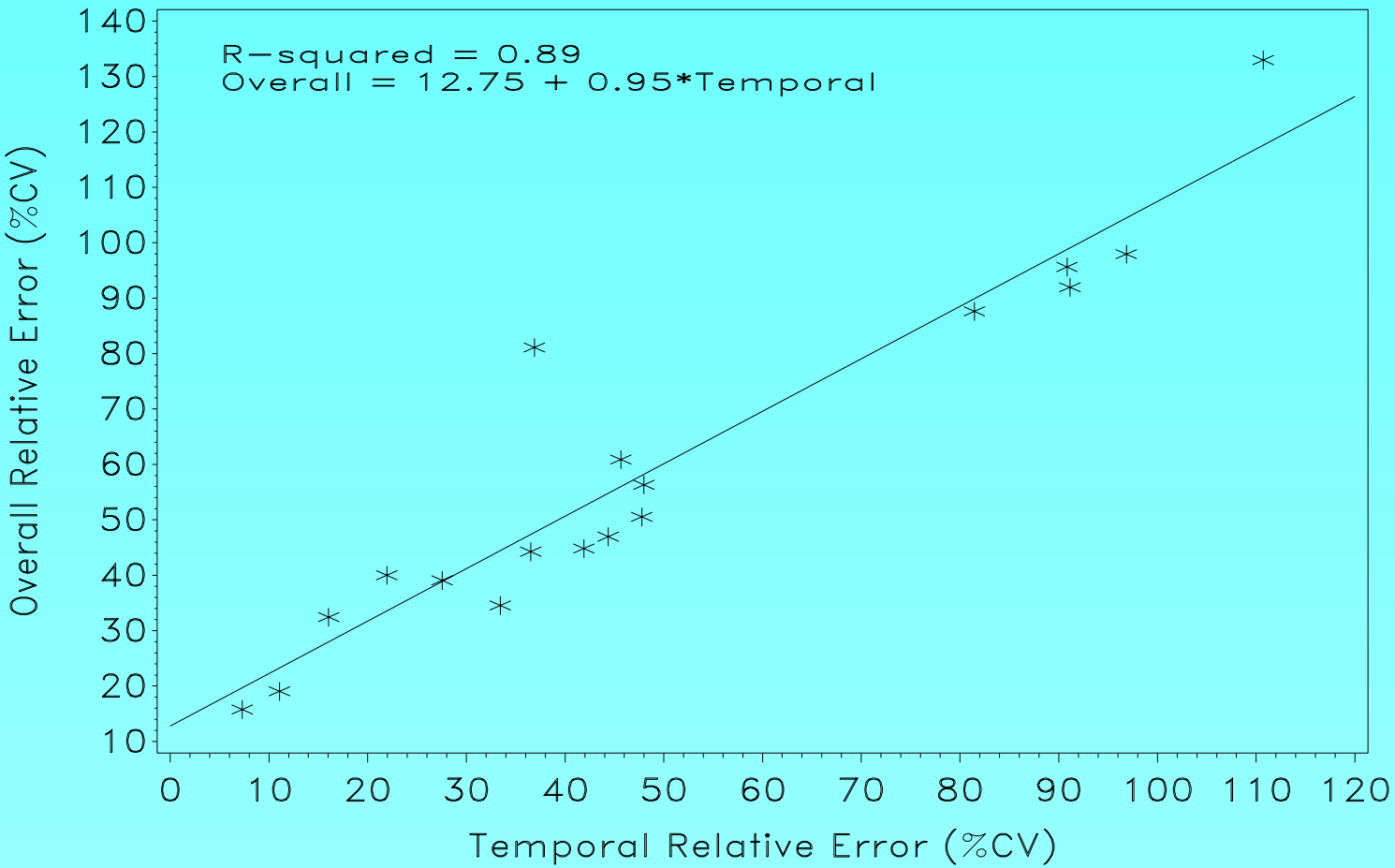


Variability = analytical



Overall ambient air toxics monitoring data variability versus Temporal variability.

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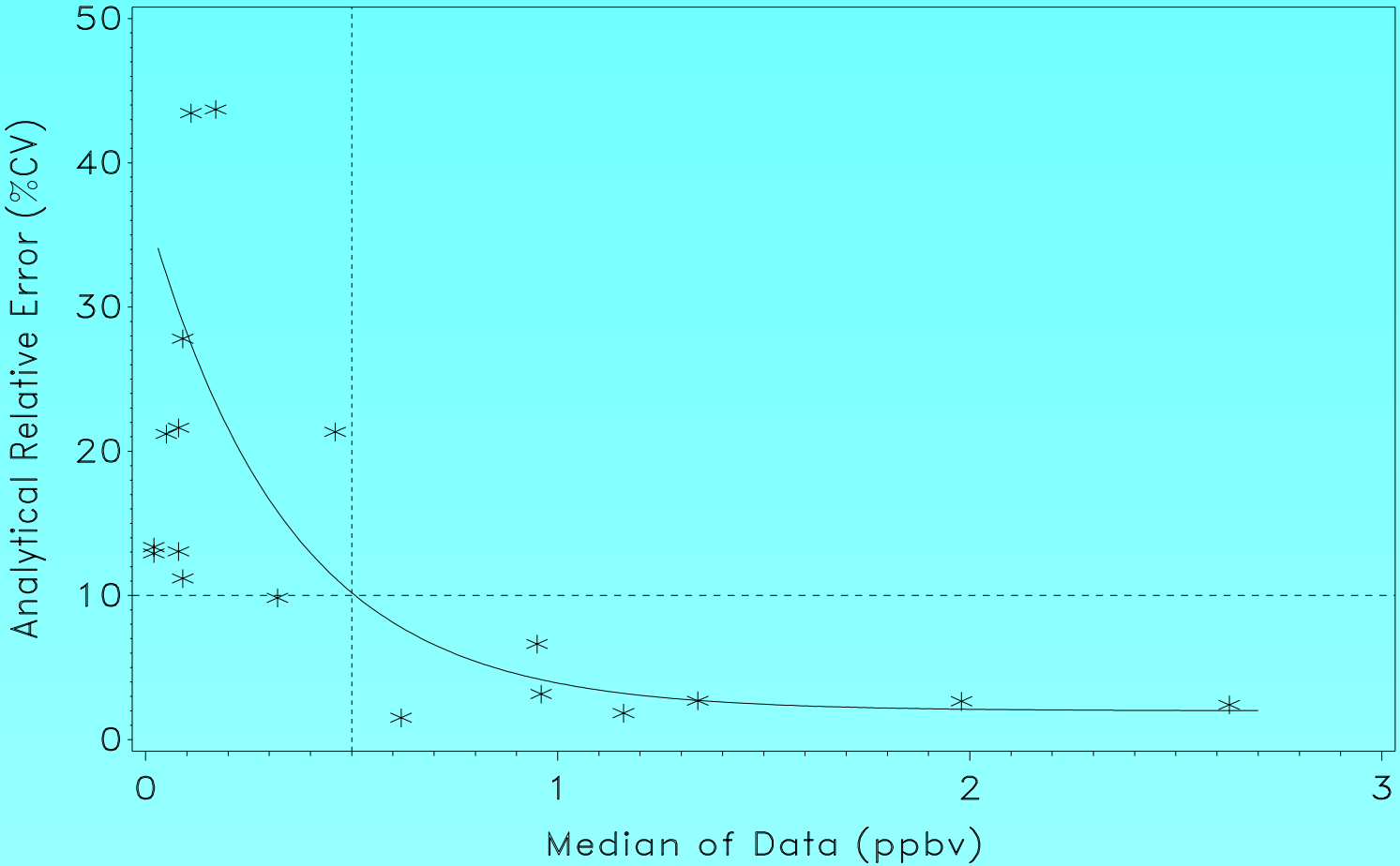


Analytical variability in ambient air toxics monitoring data versus ambient concentration levels.

Summary of Findings

- Environmental variability is much more significant than monitoring uncertainty in many cases.
- Overall data variation is mostly driven by temporal variability.
- At low enough ambient levels, environmental components of variability tend to go away and monitoring uncertainty, particularly analytical relative error, can take over.

Sampling Frequency Recommendations Based on Estimating the Mean-Variance Relationship

Specify a measure of the precision of the AA estimate.

- Coefficient of variation (CV)

$$CV_{AA} = \frac{\sigma / \sqrt{n}}{\mu} \qquad \text{(Eq. 1)}$$

Establish the relationship between σ and μ.

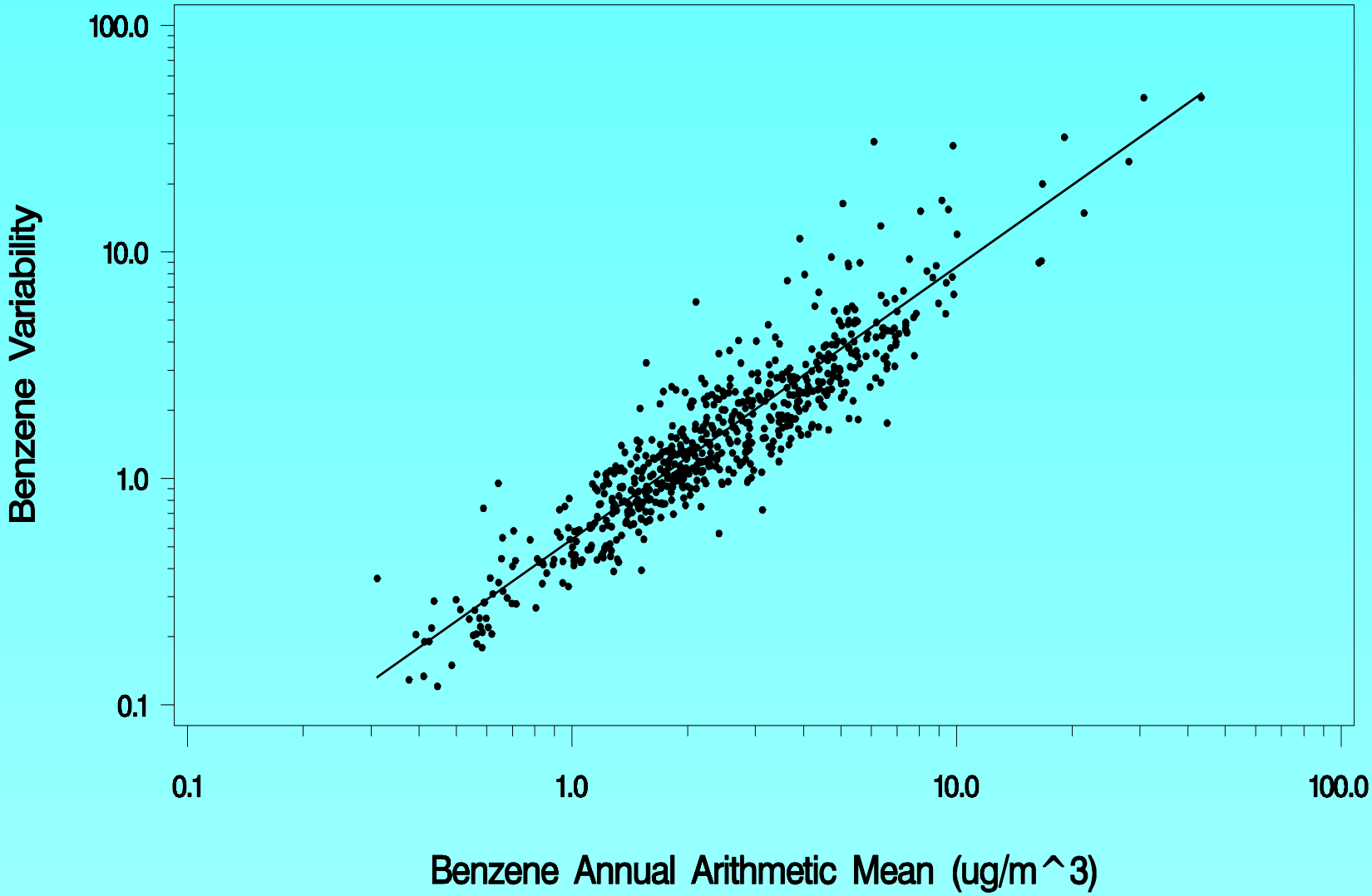
- Assuming a log-linear relationship implies:

$$\ln(\sigma) = \ln(a) + b*\ln(\mu)$$

or (Eq. 2)

$$\sigma = a\ \mu^b$$

- Weighted least squares regression; supporting graphical evidence/summaries



Scatter plots of environmental variability versus ambient concentration level, benzene.

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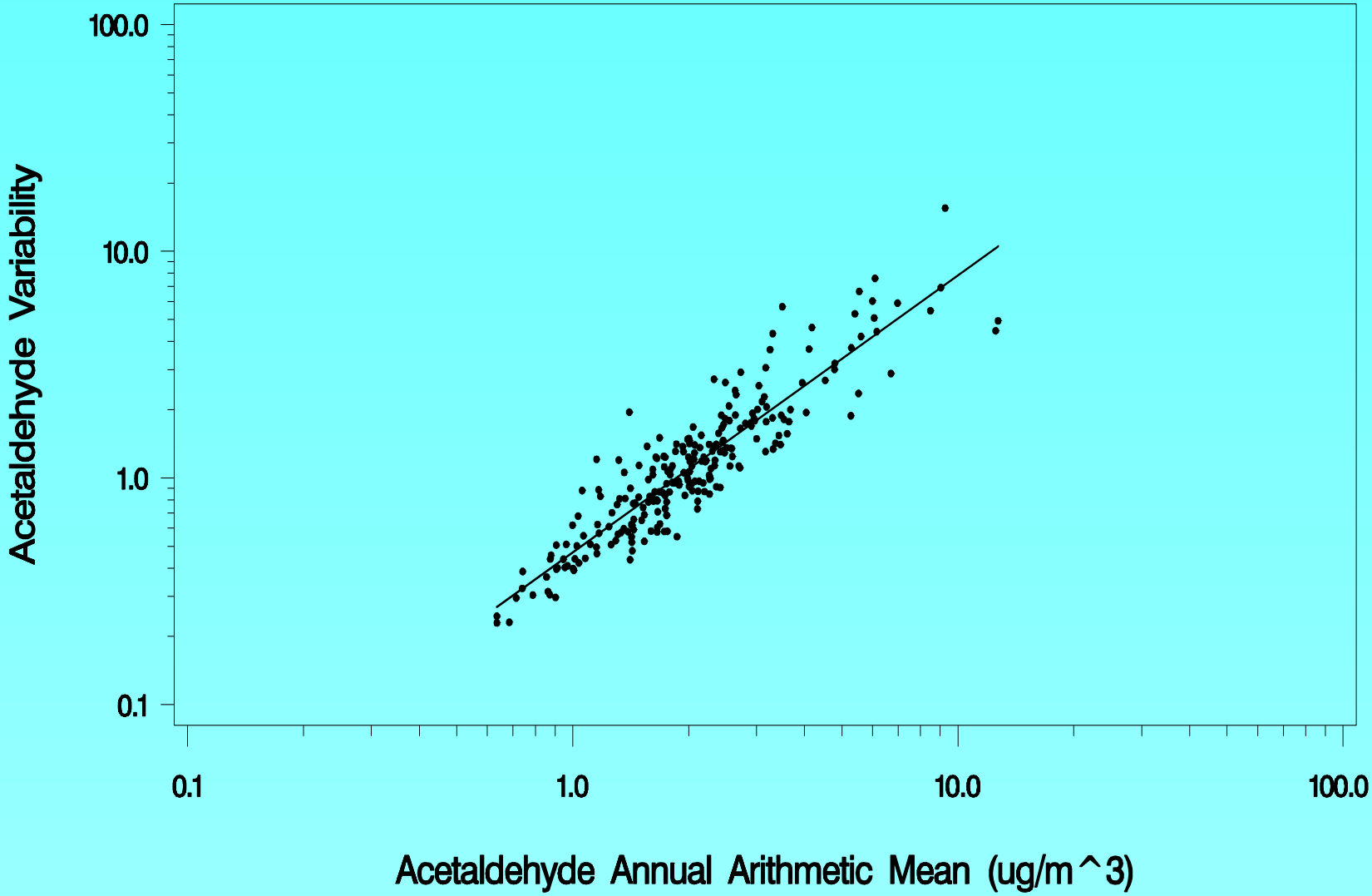

Scatter plots of environmental variability versus ambient concentration level, acetaldehyde.

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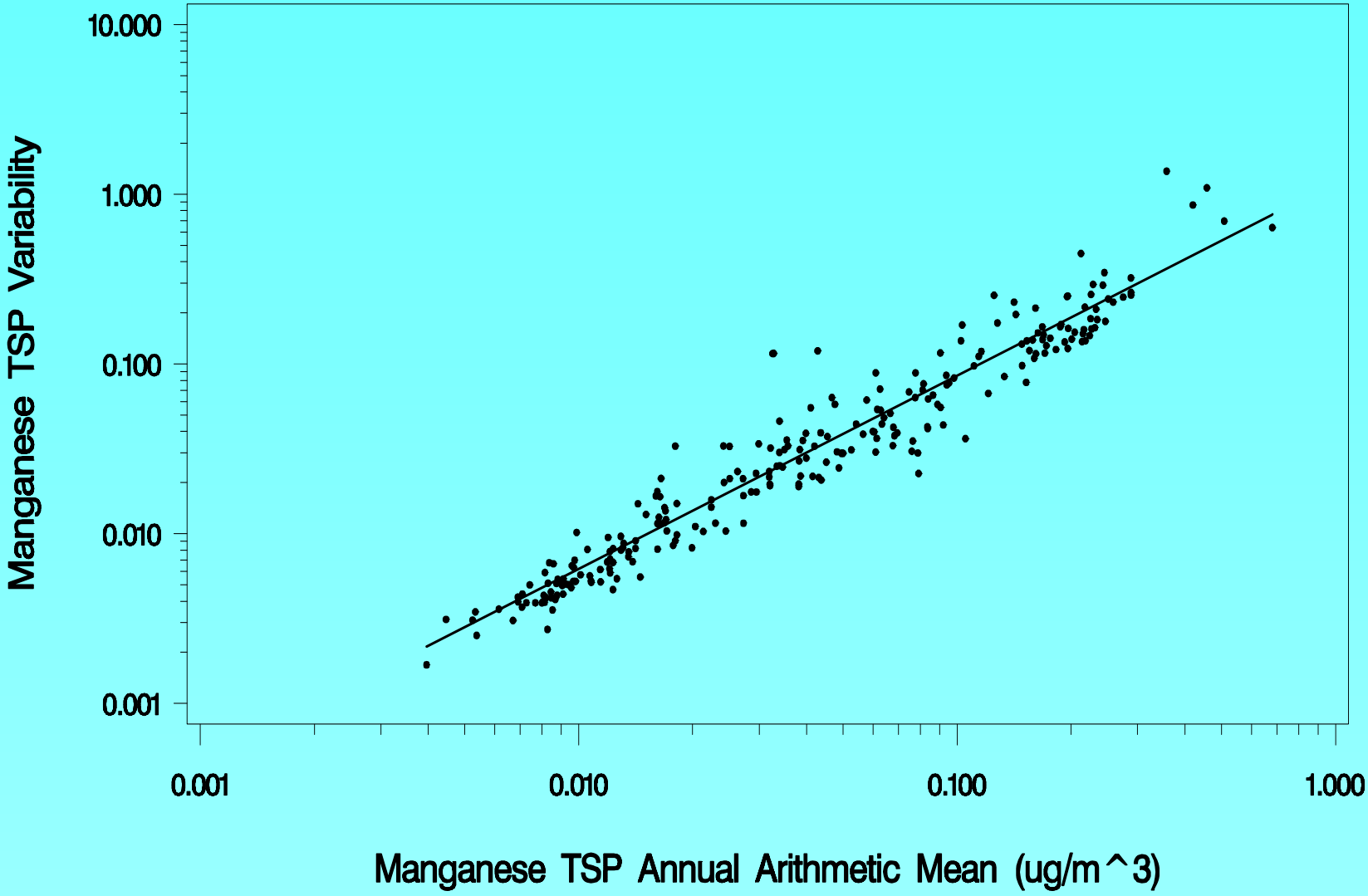

Scatter plots of environmental variability versus ambient concentration level, manganese (tsp).

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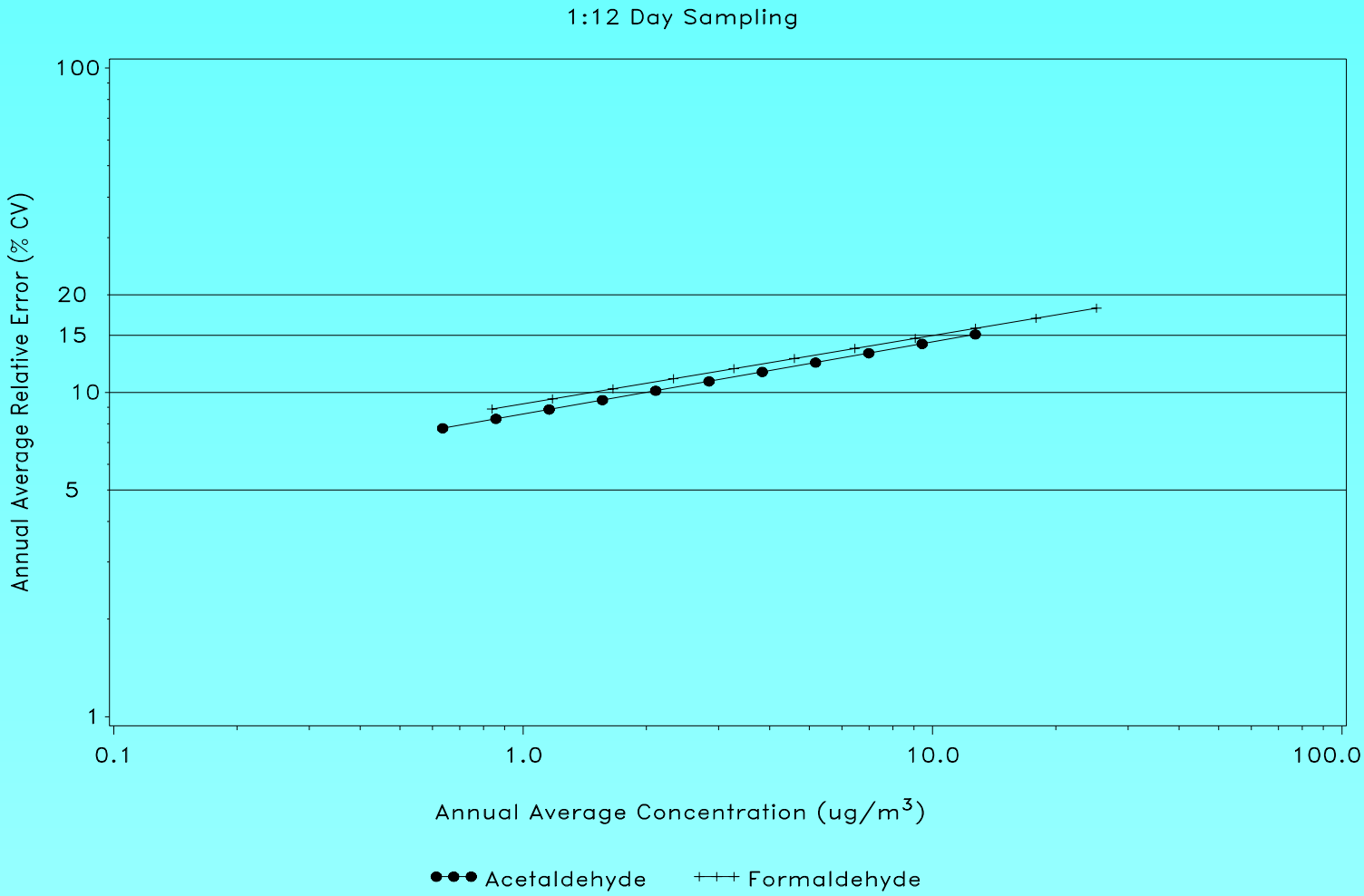
Calculate precision (CV_{AA}) as a function of sampling frequency and mean ambient level.

- Substituting Eq. 2 into Eq. 1 gives:

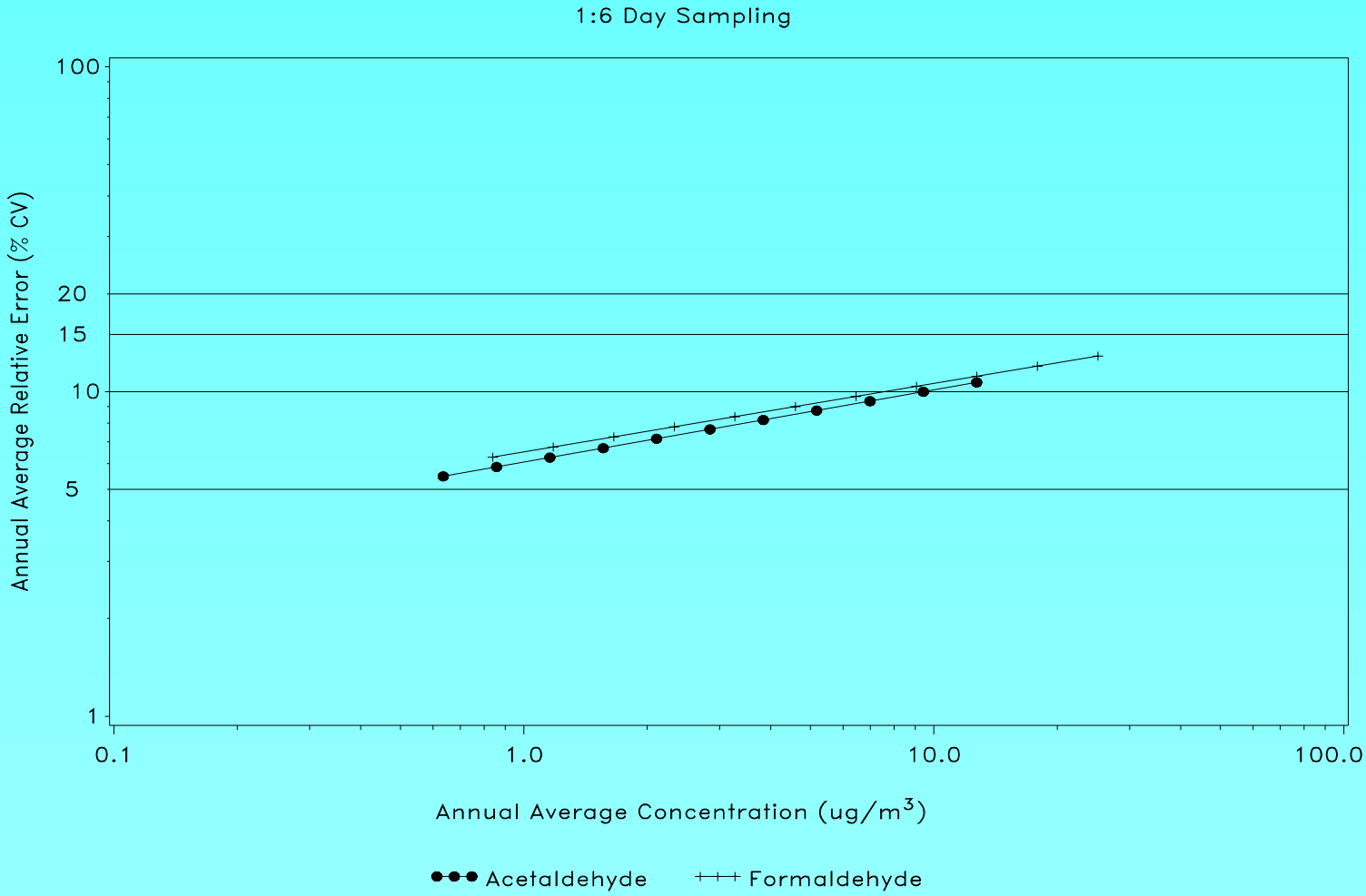
$$CV_{AA} = \frac{a\mu^{b} \Big/ \sqrt{n}}{\mu} = \frac{a}{\sqrt{n}}\mu^{b-1} \qquad \text{(Eq. 3)}$$

- Example of Eq. 3, benzene at 1:6 day sampling

$$\hat{CV}_{AA} = \frac{0.54}{\sqrt{n}}\mu^{0.2} = \frac{0.54}{\sqrt{60}}\mu^{0.2} = 0.07\mu^{0.2} \qquad \text{(Eq. 4)}$$



Percent relative errors of annual average estimates versus true average, 1:12 day sampling, carbonyls.



Percent relative errors of annual average estimates versus true average, 1:6 day sampling, carbonyls.

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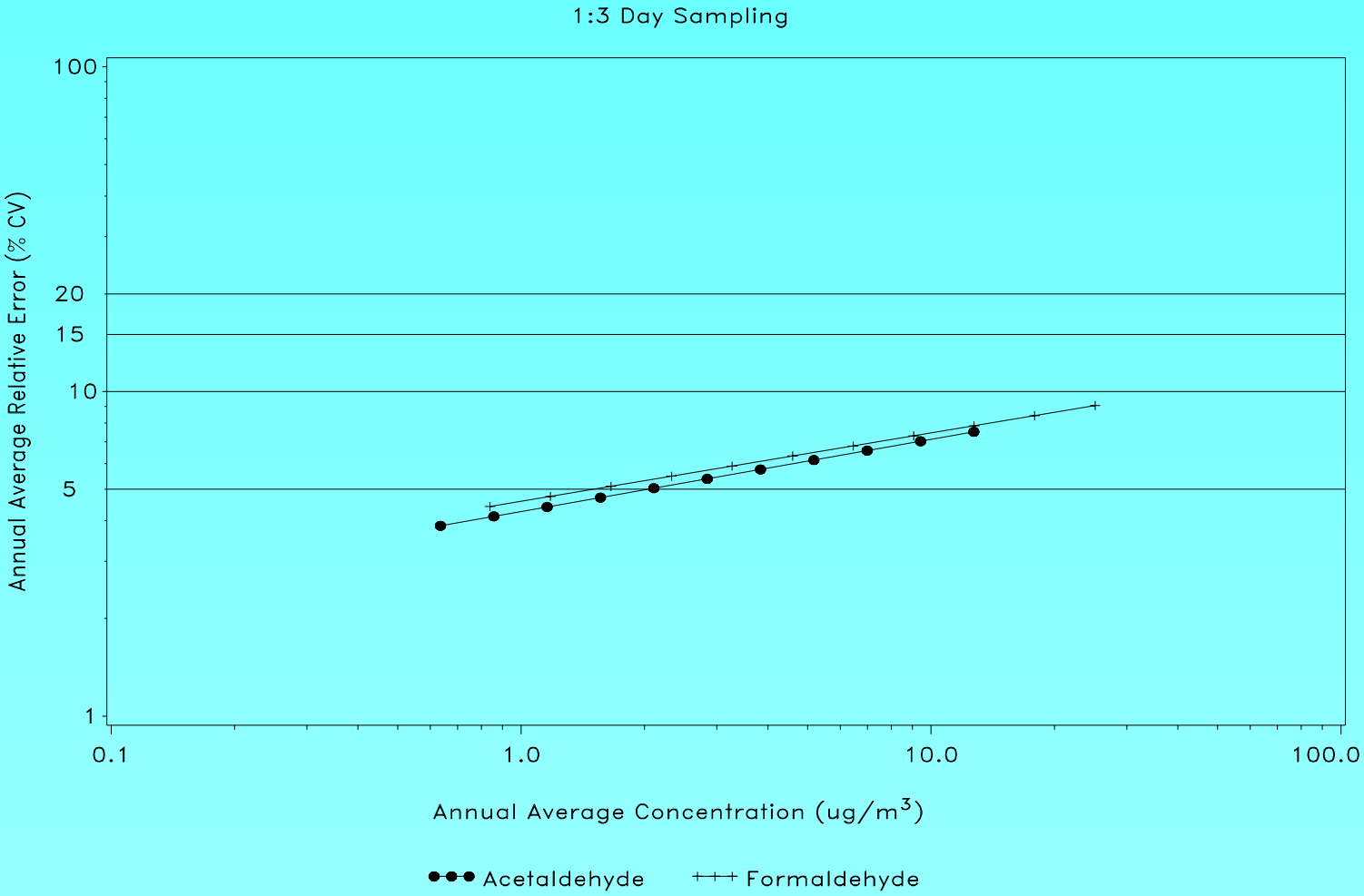
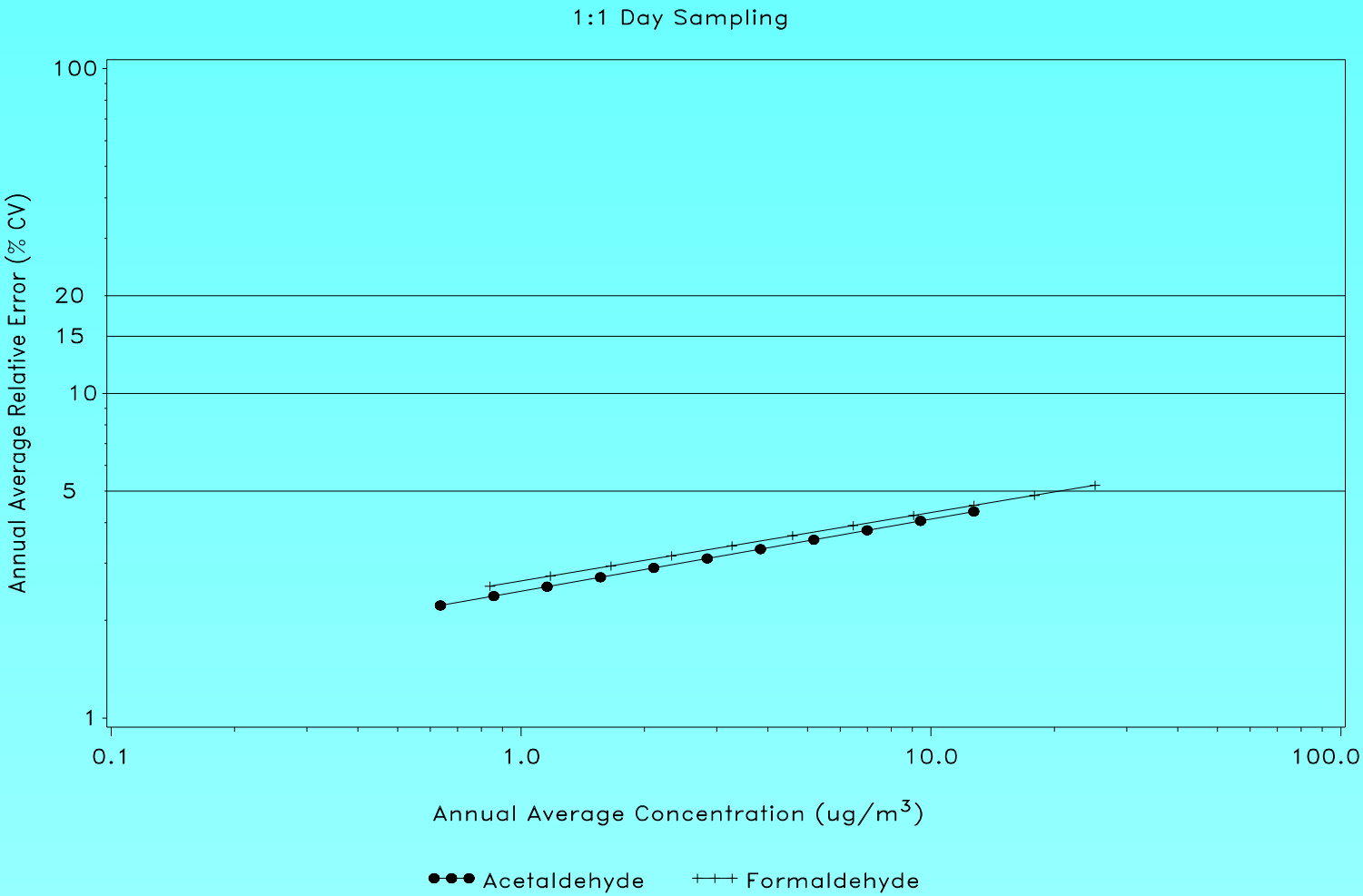
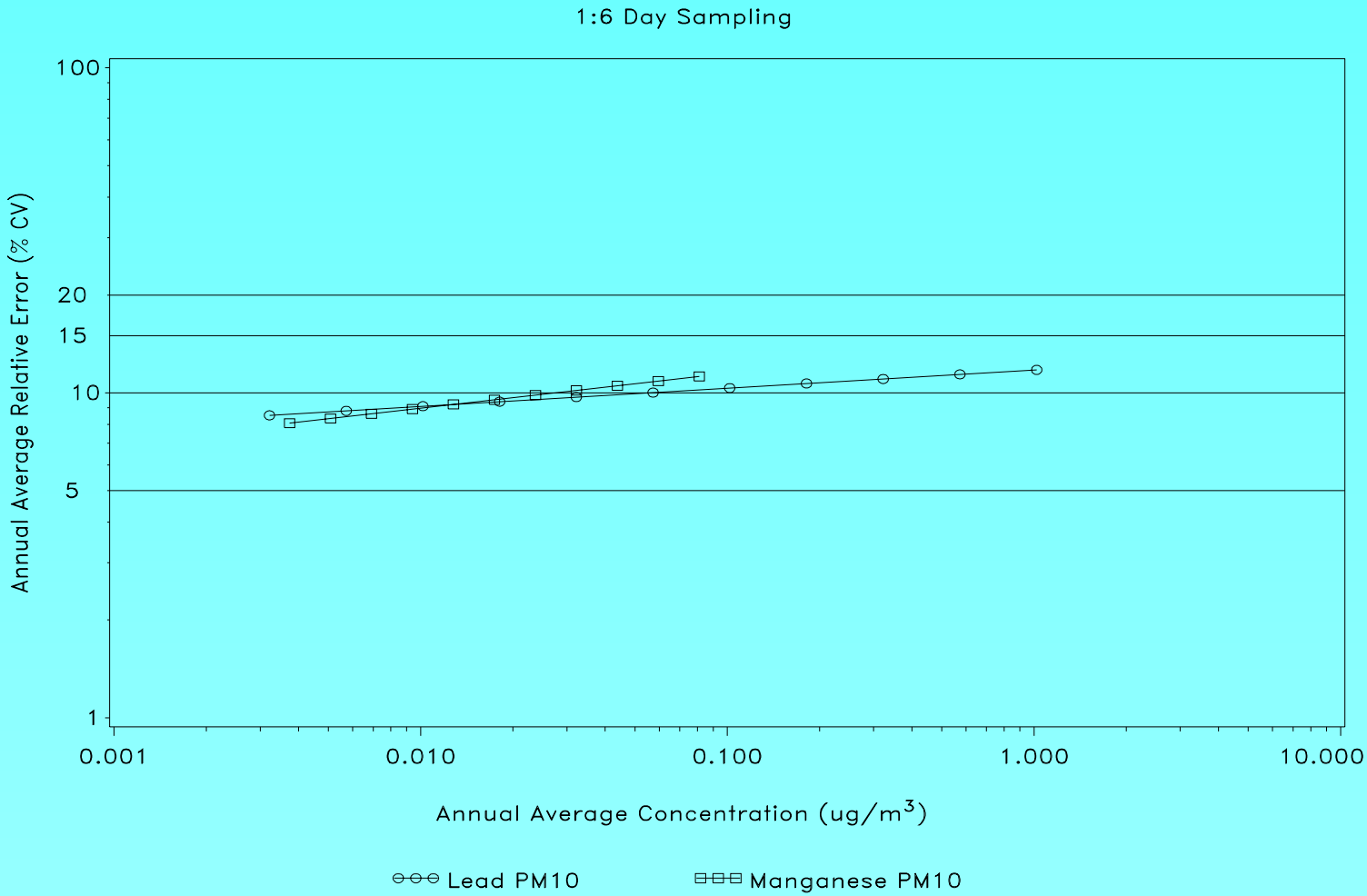


Percent relative errors of annual average estimates versus true average, 1:3 day sampling, carbonyls.



Percent relative errors of annual average estimates versus true average, 1:1 day sampling, carbonyls.



Percent relative errors of annual average estimates versus true average, 1:6 day sampling, metals (pm10).

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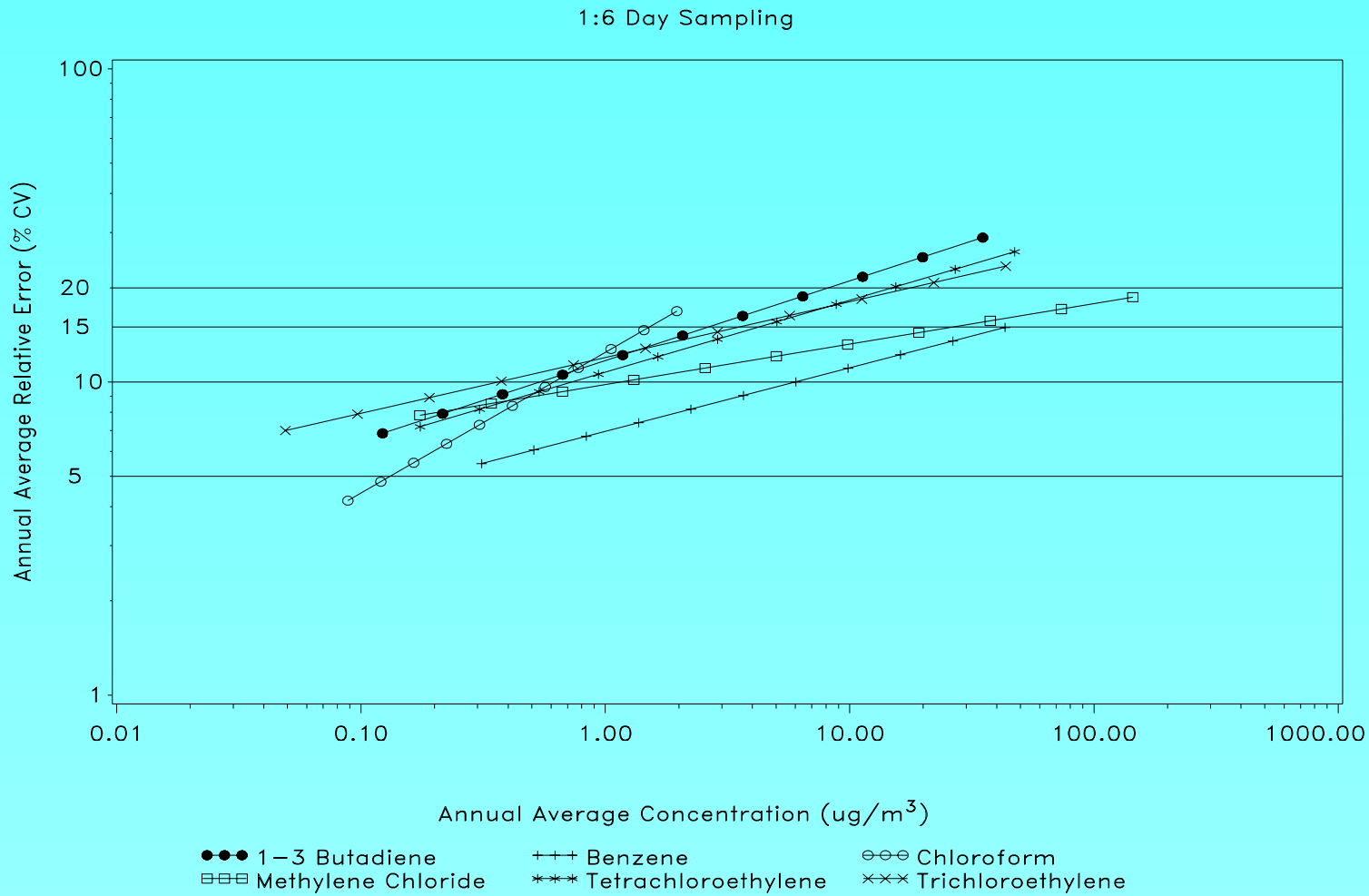

Percent relative errors of annual average estimates versus true average, 1:6 day sampling, VOCs.

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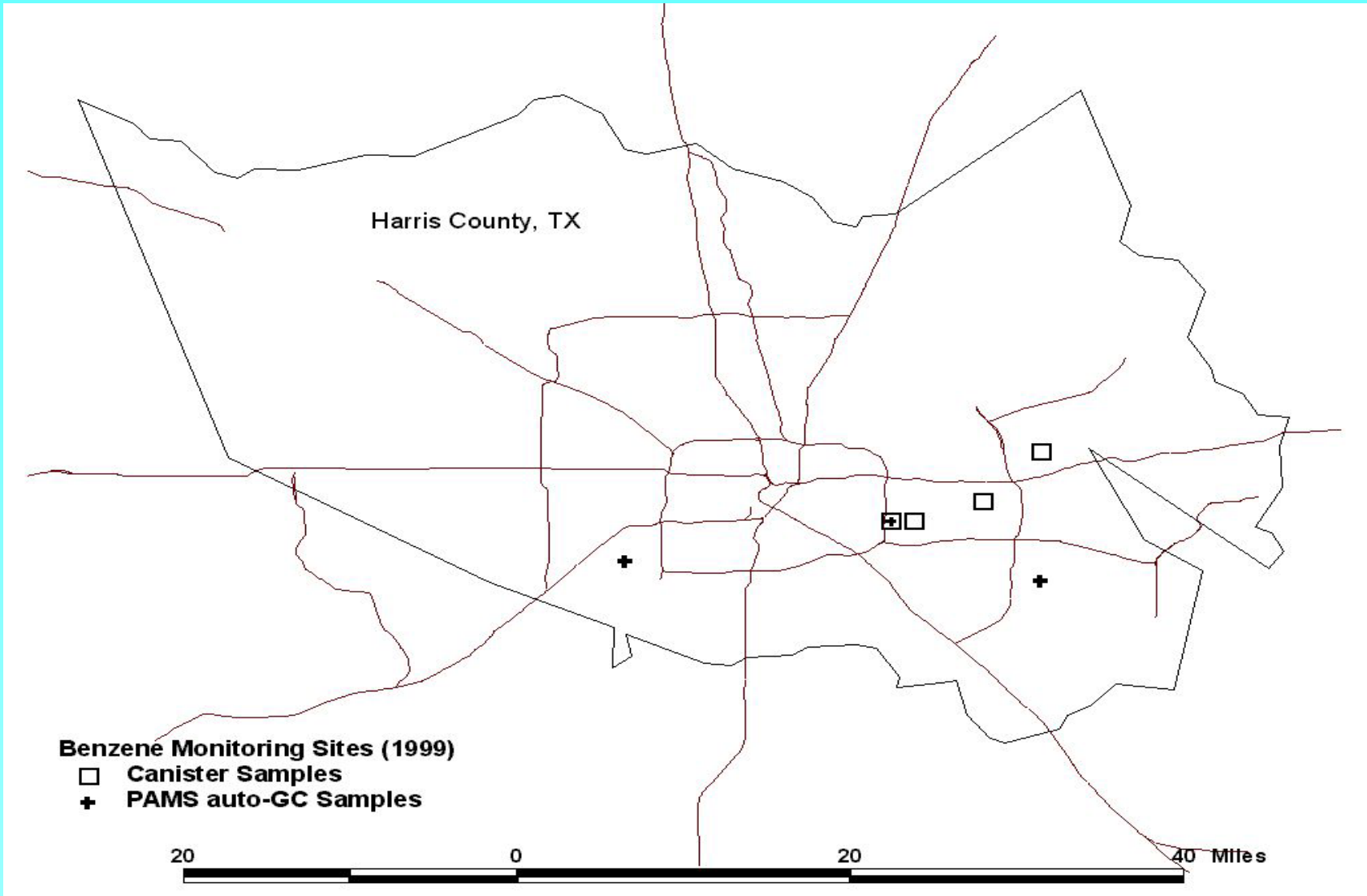
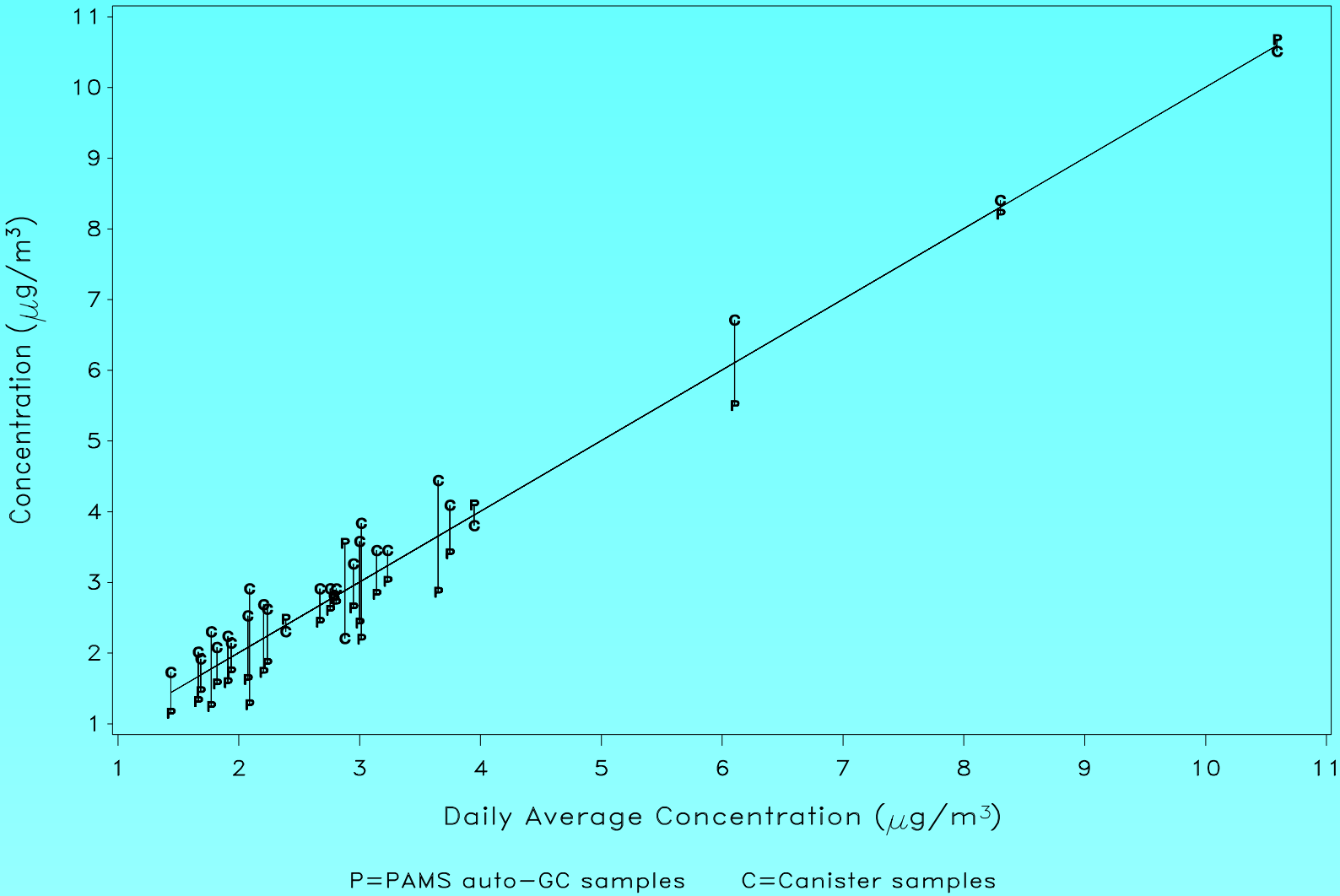
Monitoring Technologies: Bias

Bias Between Technologies

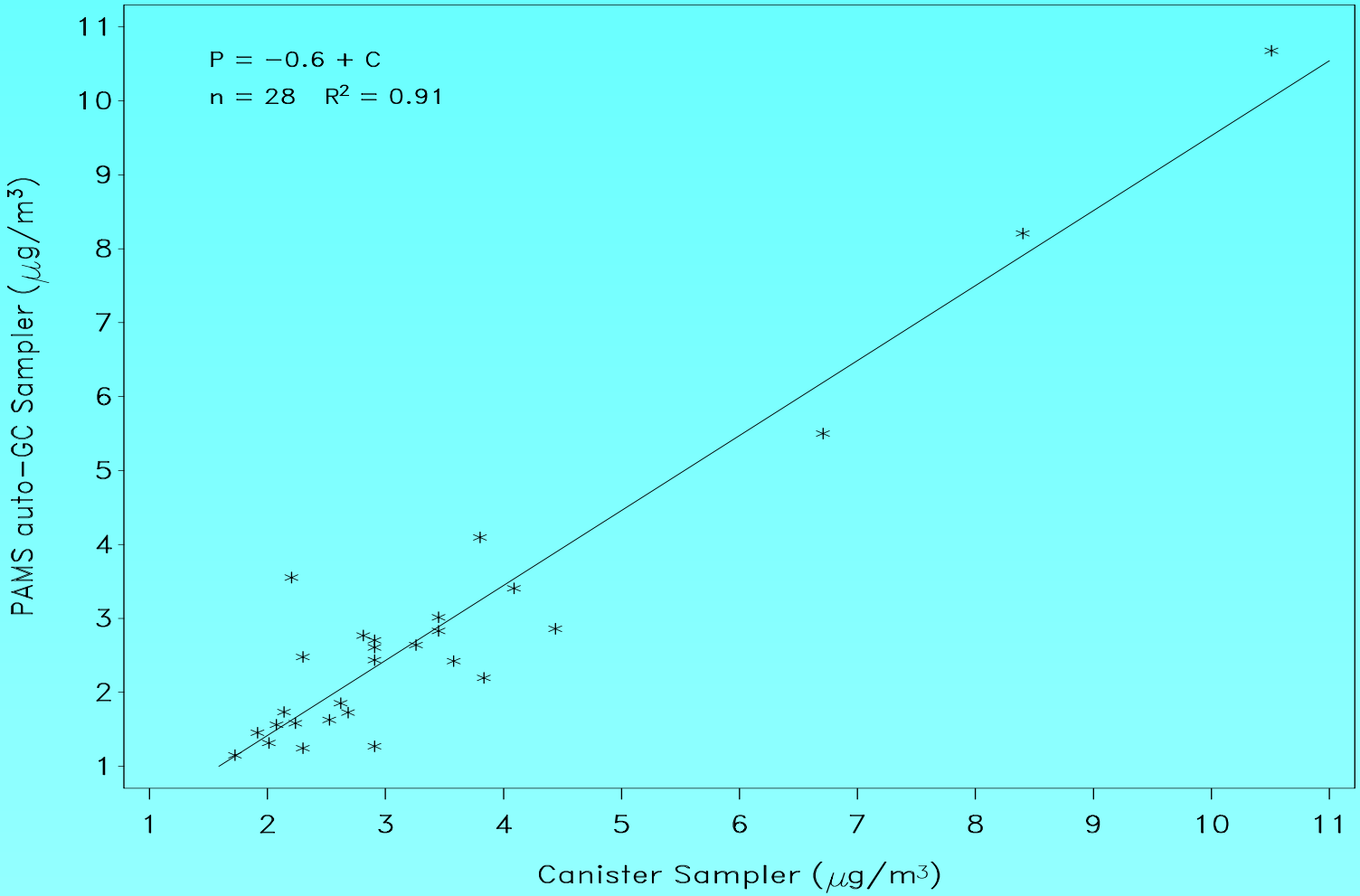
- Data: 7 monitors, 6 sites (one co-located site); 1999; benzene \ 24-hour canister data and PAMS 1-hour auto-GC data
- 24-hour canister monitors recording higher concentrations than the PAMS monitors
  - Co-located monitors (one PAMS and one 24-hour canister) recording very different measurements
- Tom Porter of Texas Natural Resource Conservation Commission confirmed:
  - Archive data valid; consistent differences due to differences in monitoring technologies



Benzene monitoring sites in Harris County, Texas



Comparison of benzene concentrations, co-located PAMS data versus 24-hour canister data



Comparison of co-located PAMS data versus 24-hour canister data

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Monitoring Data Inter-relationships

Spatial and Inter-compound Correlations

Spatial or Site-to-Site Correlations

- *To what degree does site-to-site (spatial) correlation exist within an urban or similar spatial scale environment?*

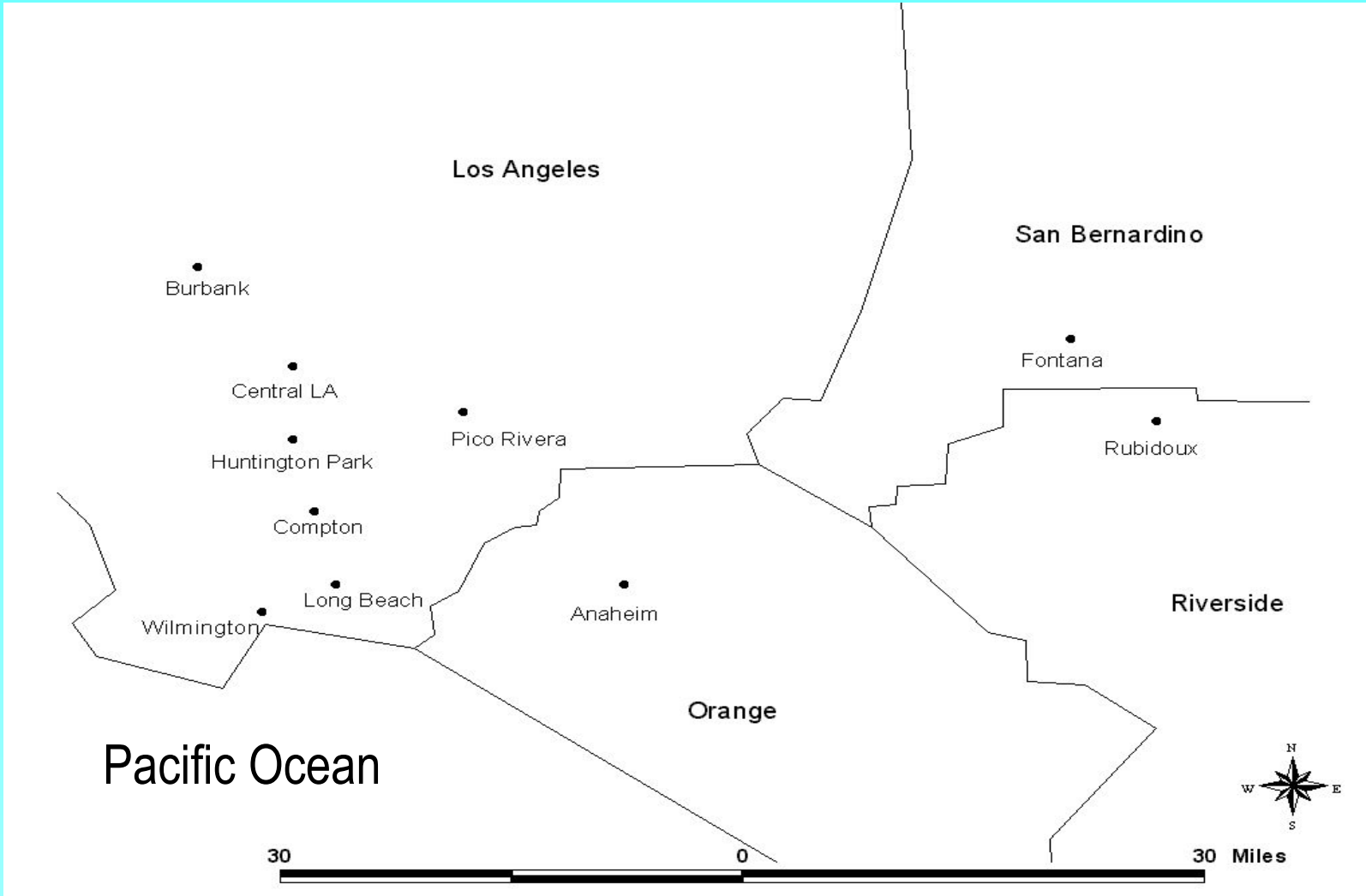
- *What are the factors that affect site-to-site correlation?*

Spatial or Site-to-Site Correlations

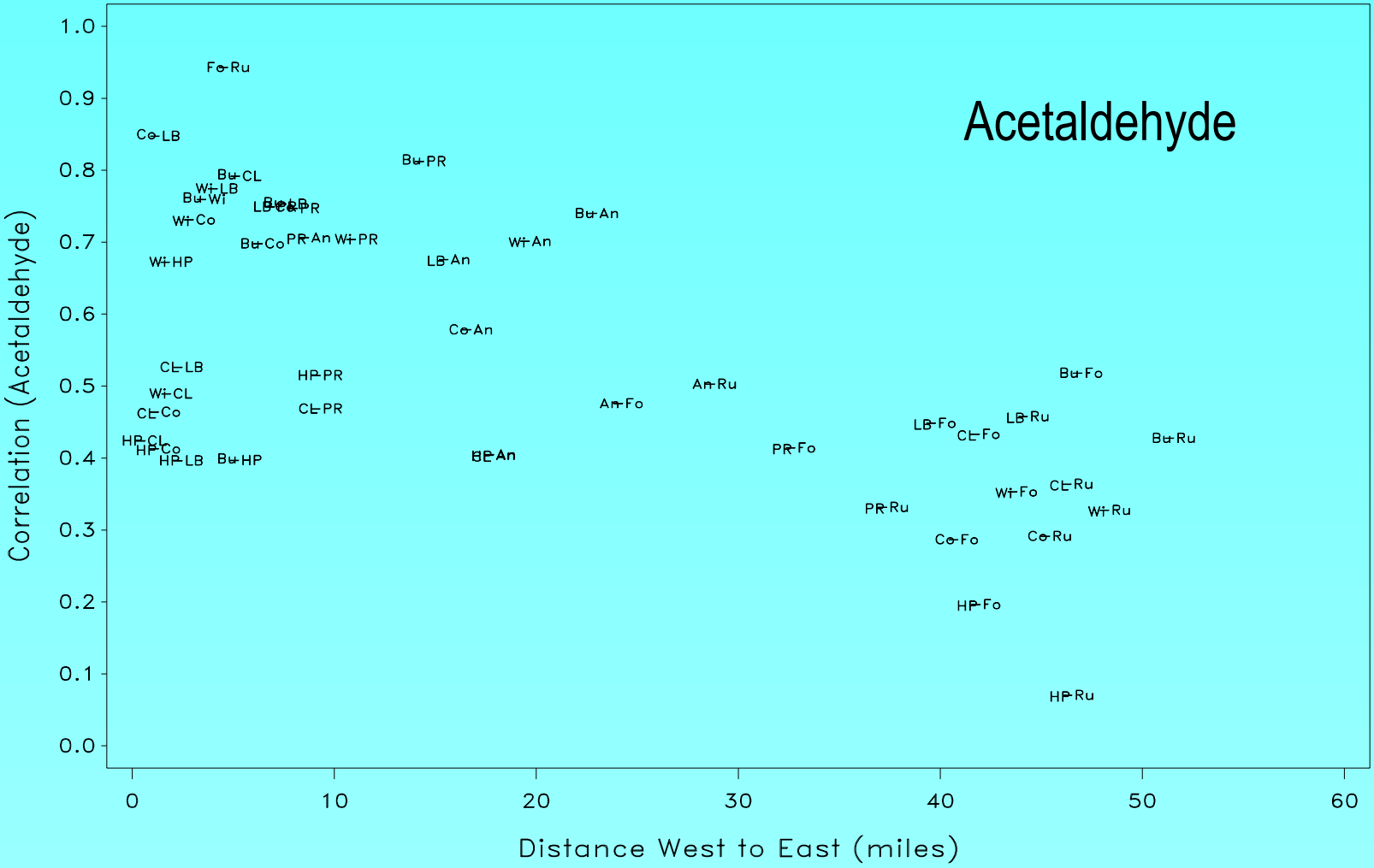
- **Data**
  - From MATES-II study (10 sites); matched measurements for same chemical compound, on same day, but from different sites; 45 unique site-to-site combinations per compound

- **Approach**
  - Calculated site-to-site correlation coefficients for each compound
  - Calculated distance between sites
  - Presented correlations versus the distance between associated sites, W to E and N to S

Map of MATES-II Monitoring Stations



Site:site correlation versus W:E distance between sites



An=Anaheim Bu=Burbank CL=Central LA Co=Compton Fo=Fontana HP=Huntington Park LB=Long Beach PR=Pico Rivera Ru=Rubidoux Wi=Wilmington

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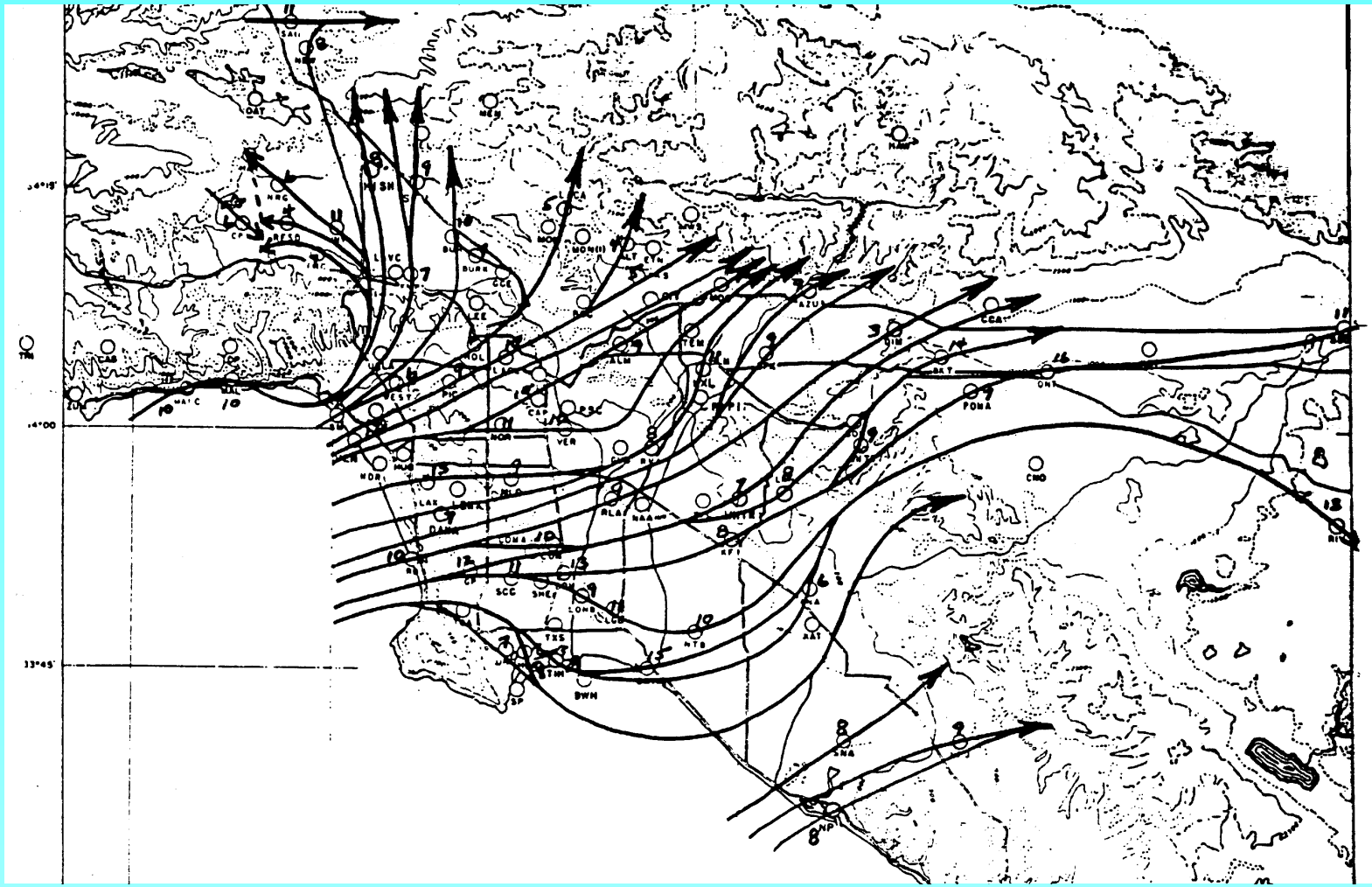
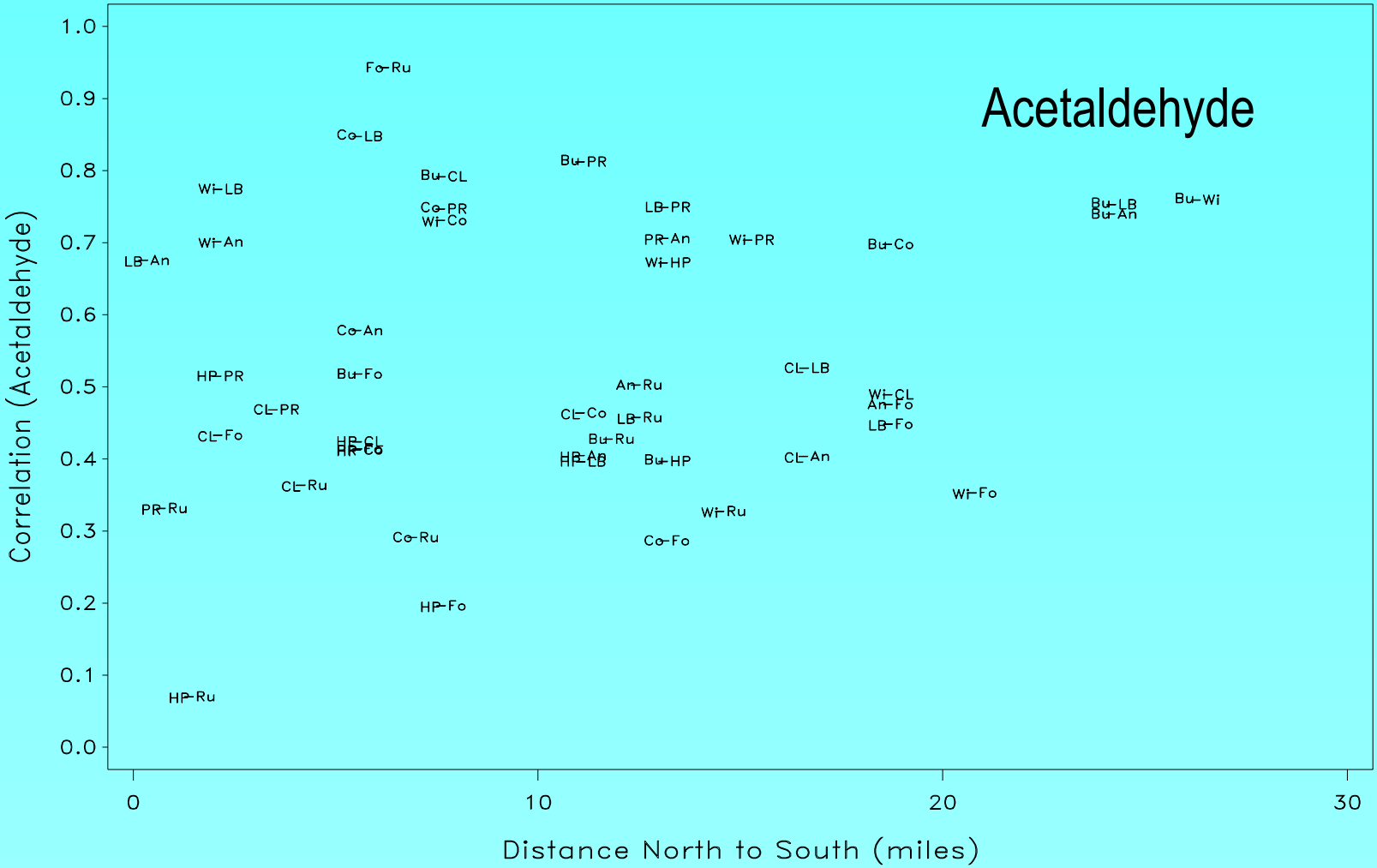
Average monthly streamlines (July at 1600 PST)



Site:site correlation versus N:S distance between sites



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Chemical Compound-to-Compound Correlations

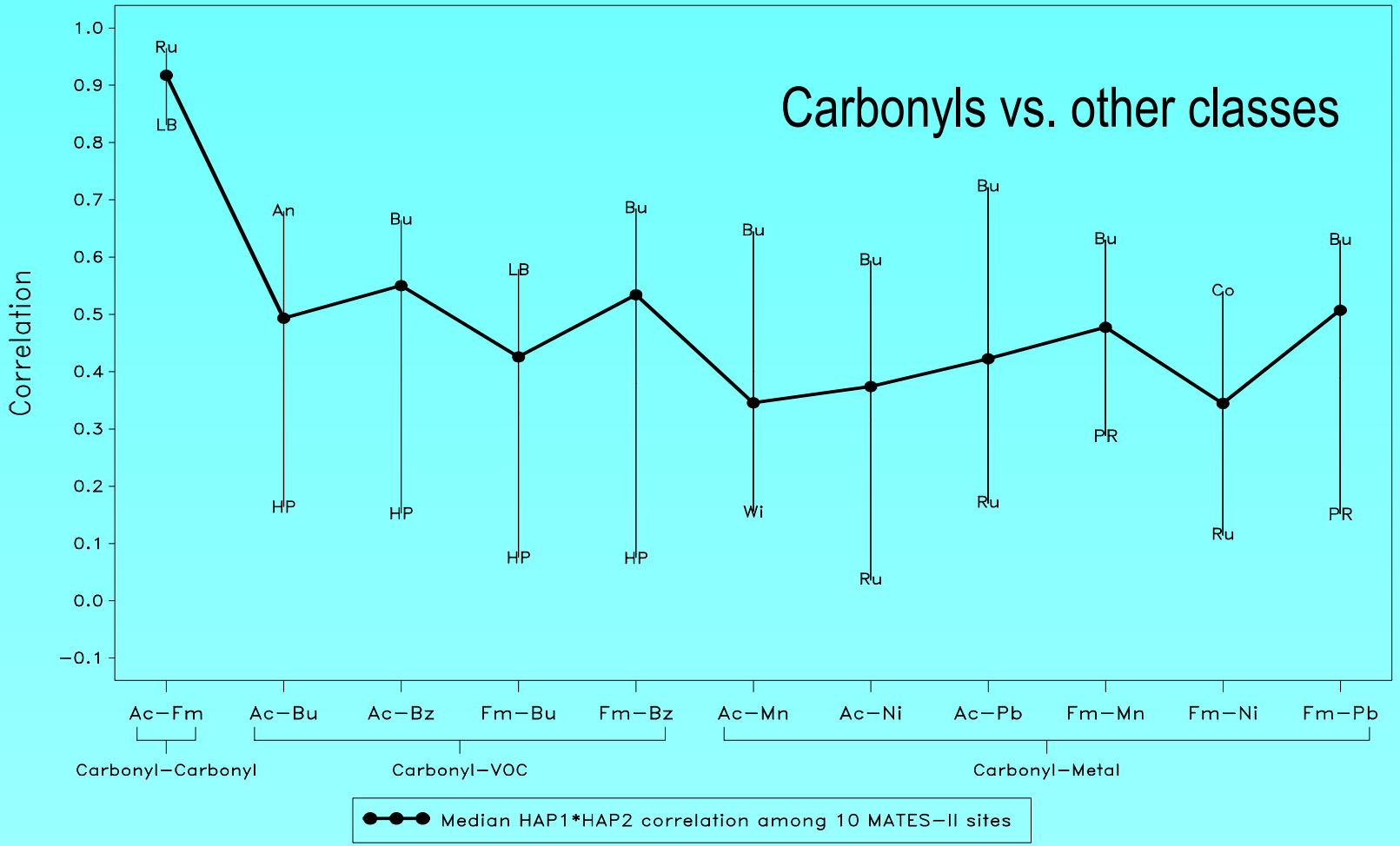
- *To what degree does chemical compound-to-compound (inter-compound) correlation exist within an urban or similar spatial scale environment?*

- *How do inter-compound correlations compare within and between chemical compound classes?*

Chemical Compound-to-Compound Correlations

- **Data**
  - From MATES-II study (10 sites); matched measurements for different chemical compounds on same day and same location; 21 distinct compound pairings per site
- **Approach**
  - Calculate inter-compound correlations for each site

Inter-compound correlation by chemical compound



Ac = acetaldehyde
Bu = 1,3-butadiene
Fm = formaldehyde
Bz = benzene

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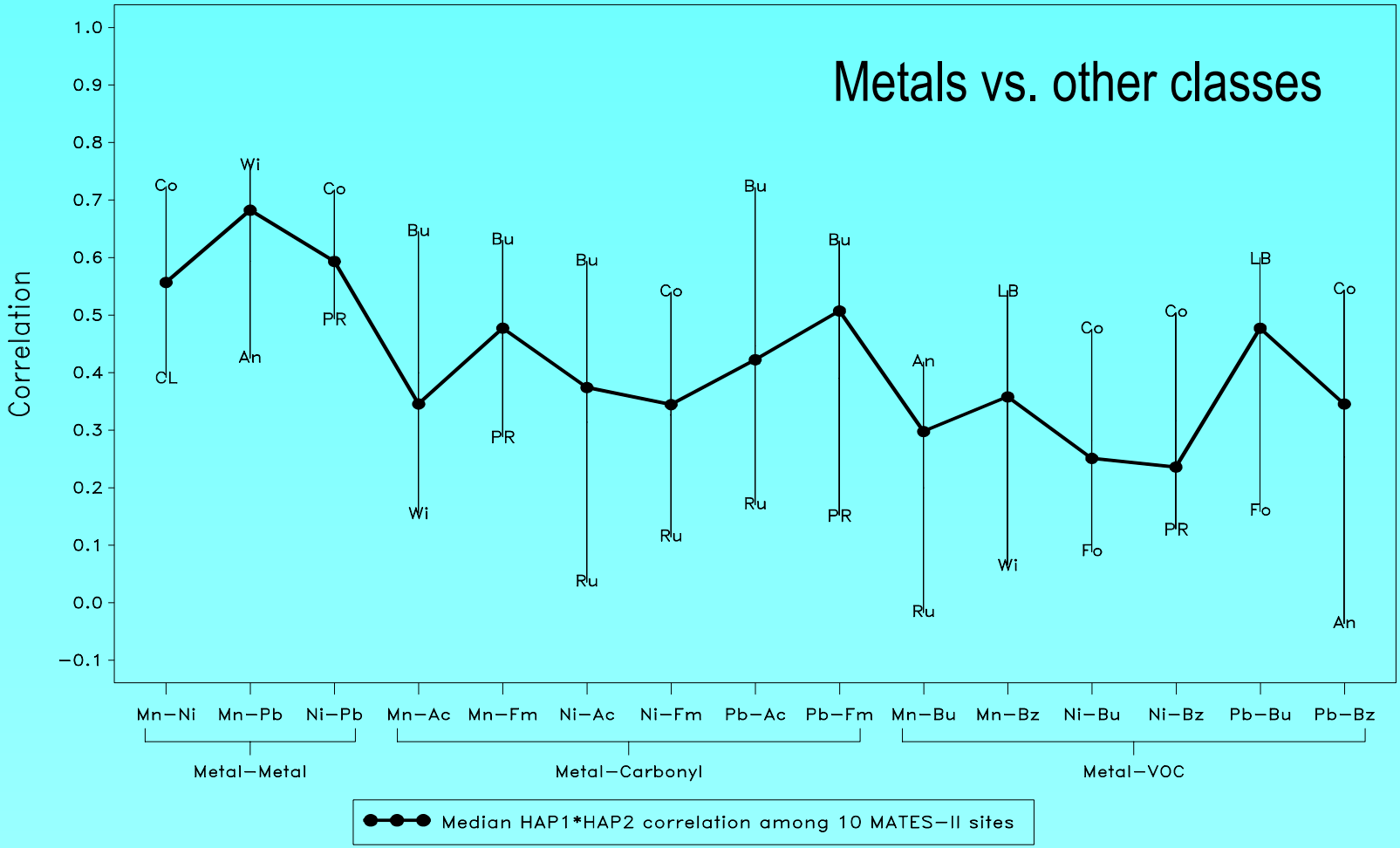
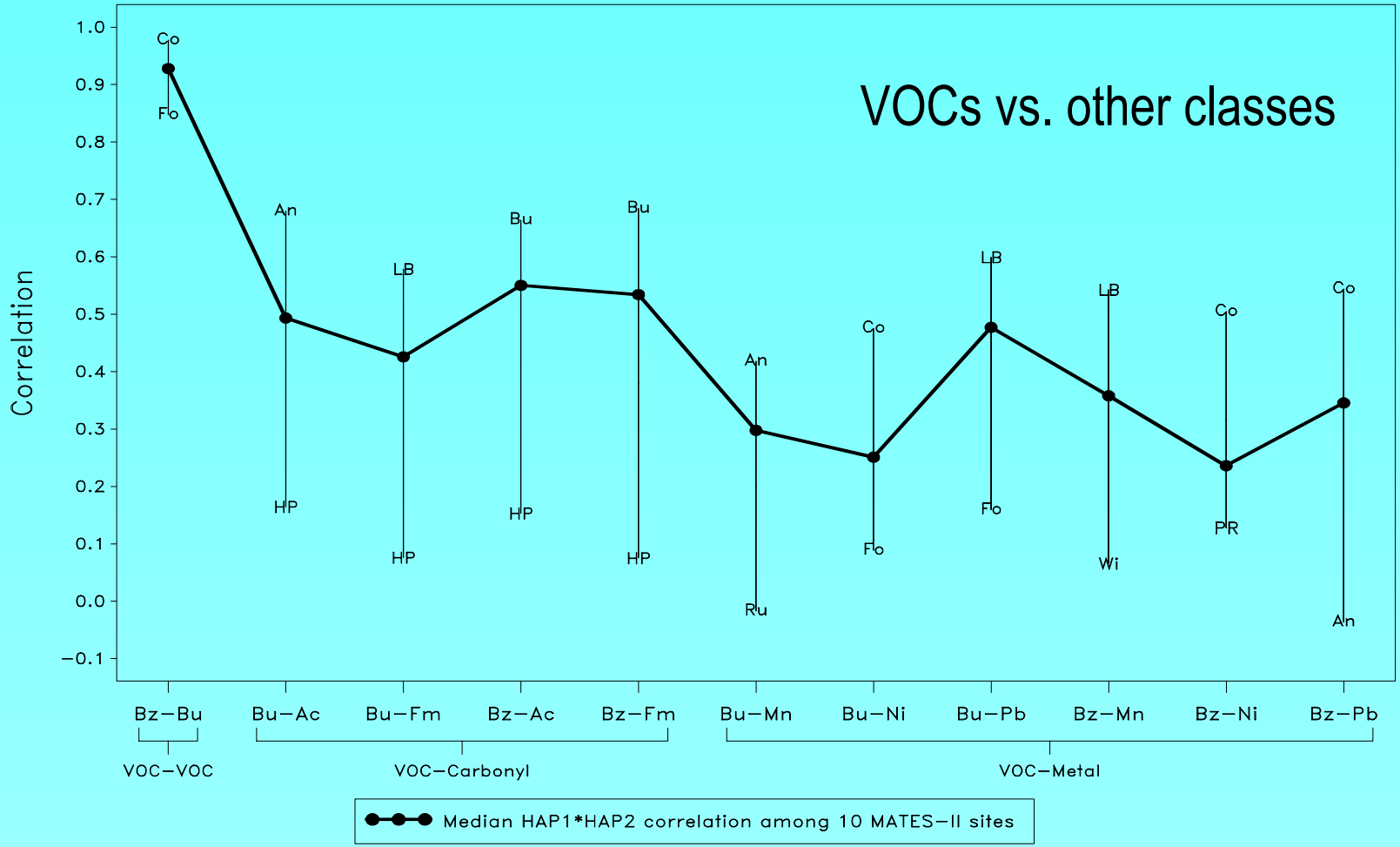
Inter-compound correlation by chemical compound



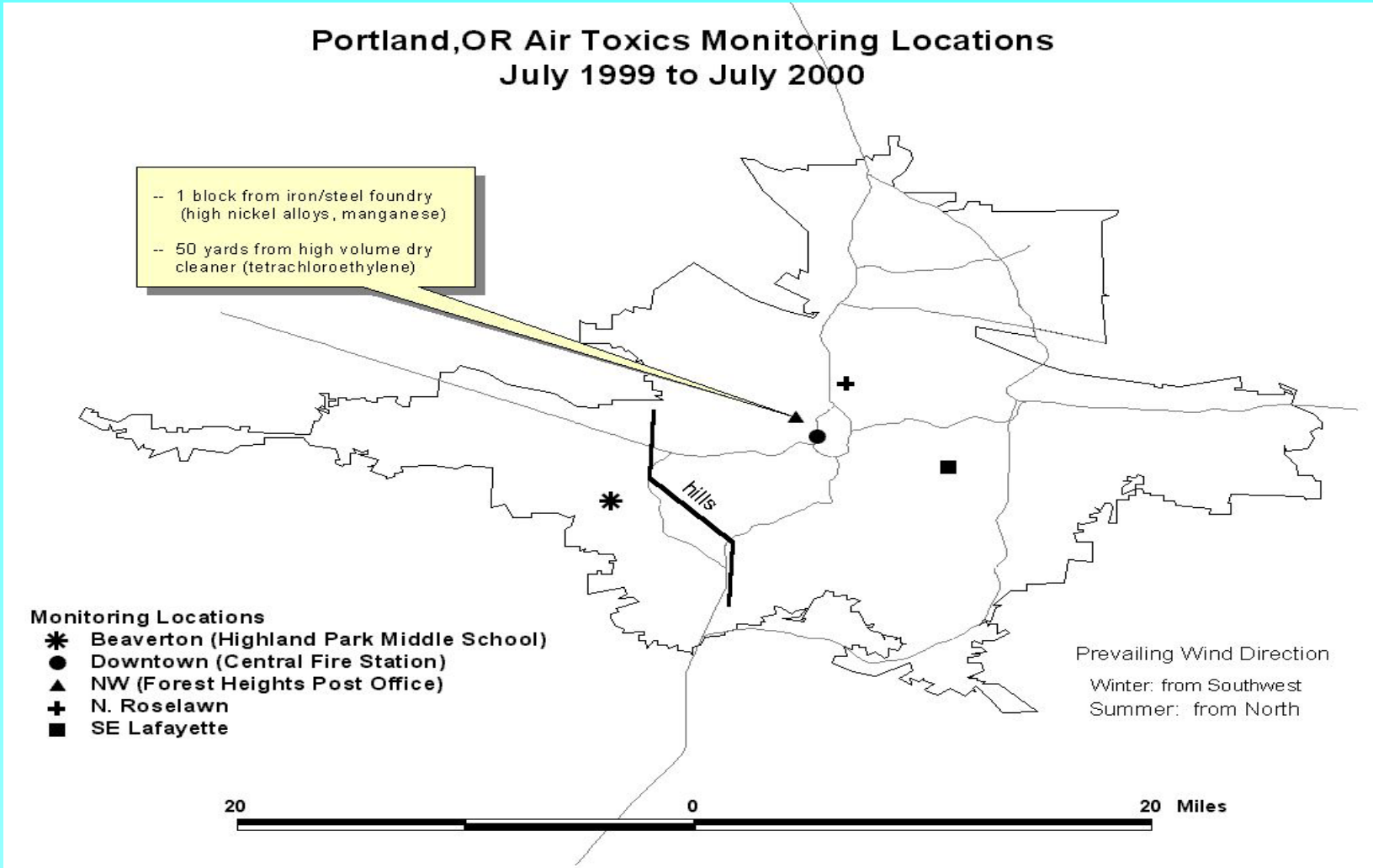
Inter-compound correlation by chemical compound



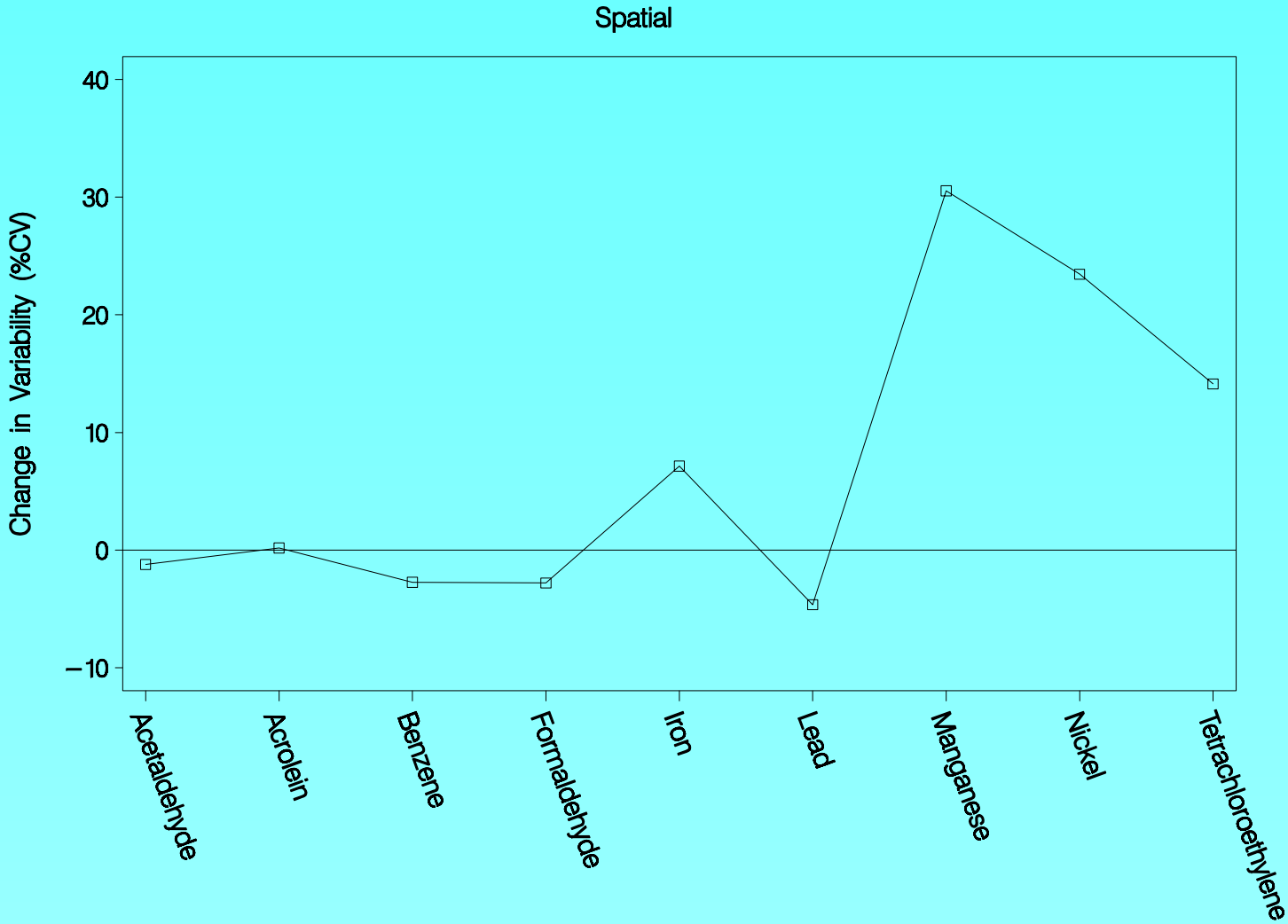
Spatial Case Studies

Case Study 1: Portland, Oregon

- **Goal**: *Demonstrate the effect of local point source emissions across a wide range of air toxics (carbonyls, metals, and VOCs).*
- Five sites; 1:6 day 24-hour samples; July 1999 to July 2000
- High tetrachloroethylene concentrations at N.W. Post Office site
- High variability (overall and spatial) for nickel, manganese, and iron
- Gregg Lande of Oregon DEQ confirmed:
  - NWPO station close to high volume dry cleaners
  - NWPO station one block from iron/steel foundry



Map of Portland, Oregon, air toxics monitoring locations and relevant information



Change in variance components in Portland, Oregon, due to removing NW Post Office station

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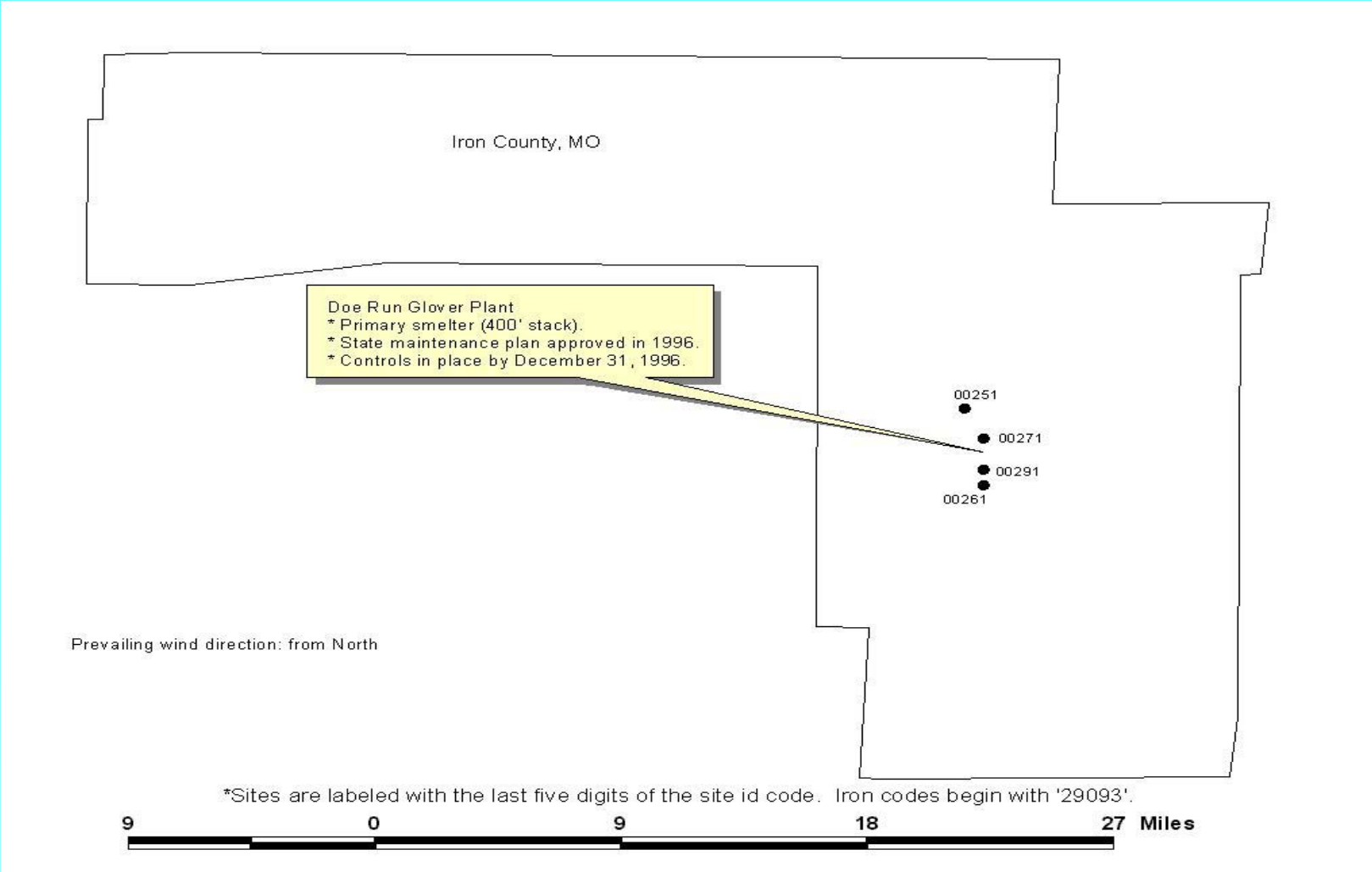
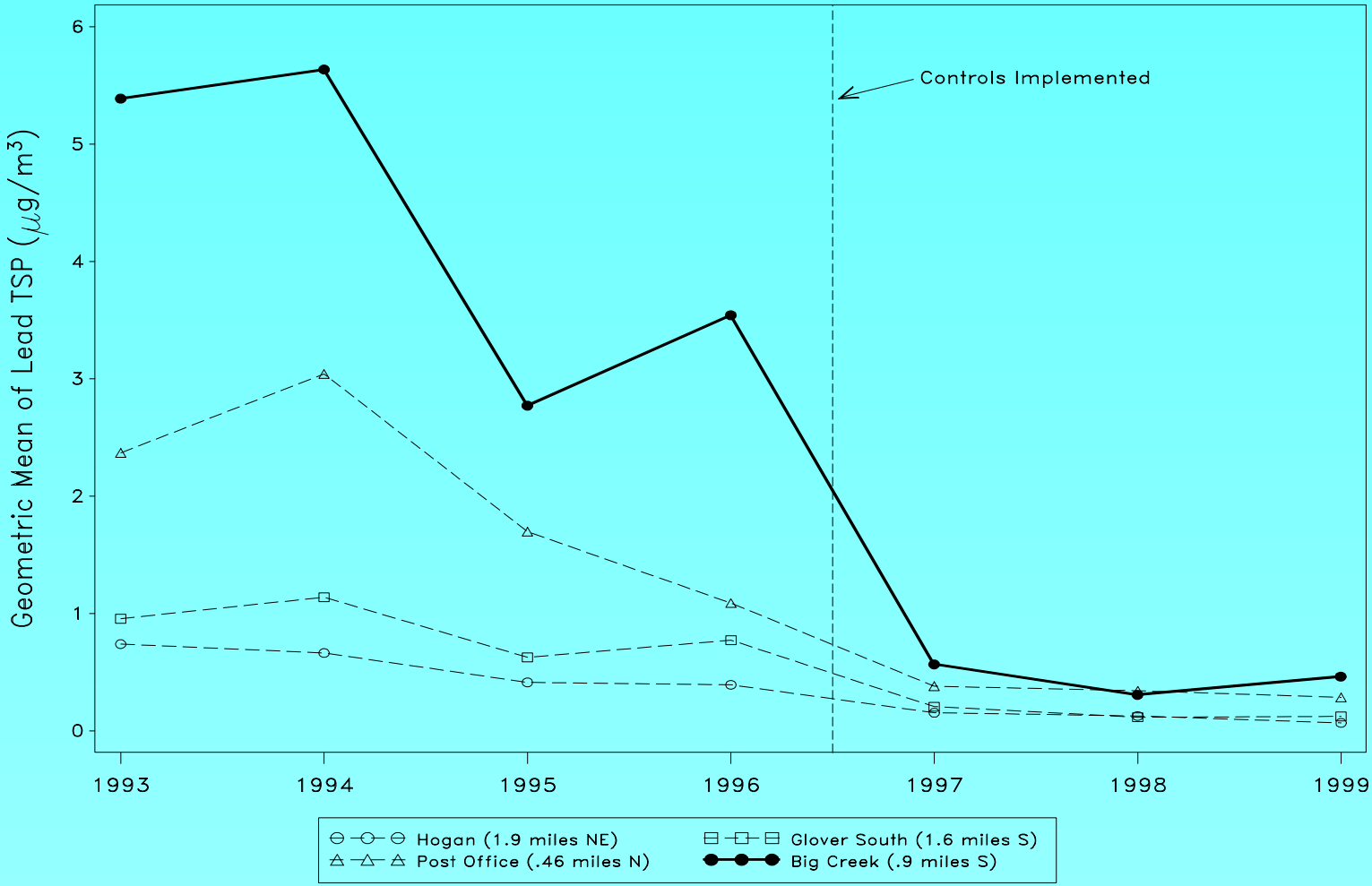
Case Study 2: Iron County, Missouri

- **Goal**: *Demonstrate the effect of local source reductions (controls) on monitoring needs.*
- Four sites; 1993 to 1999
- Don Cripe of Missouri Department of Natural Resources informed:
  - Monitors surround primary lead smelter
  - State maintenance plan approved in 1996; controls in place by December 31, 1996
- Decrease in annual average concentrations after 1996
  - Post 1996, one monitor might be sufficient



Map of lead (tsp) monitoring sites and point sources in Iron County, Missouri



Time trend of annual geometric mean lead (tsp) concentrations (μg/m³) in Iron County, Missouri, by site

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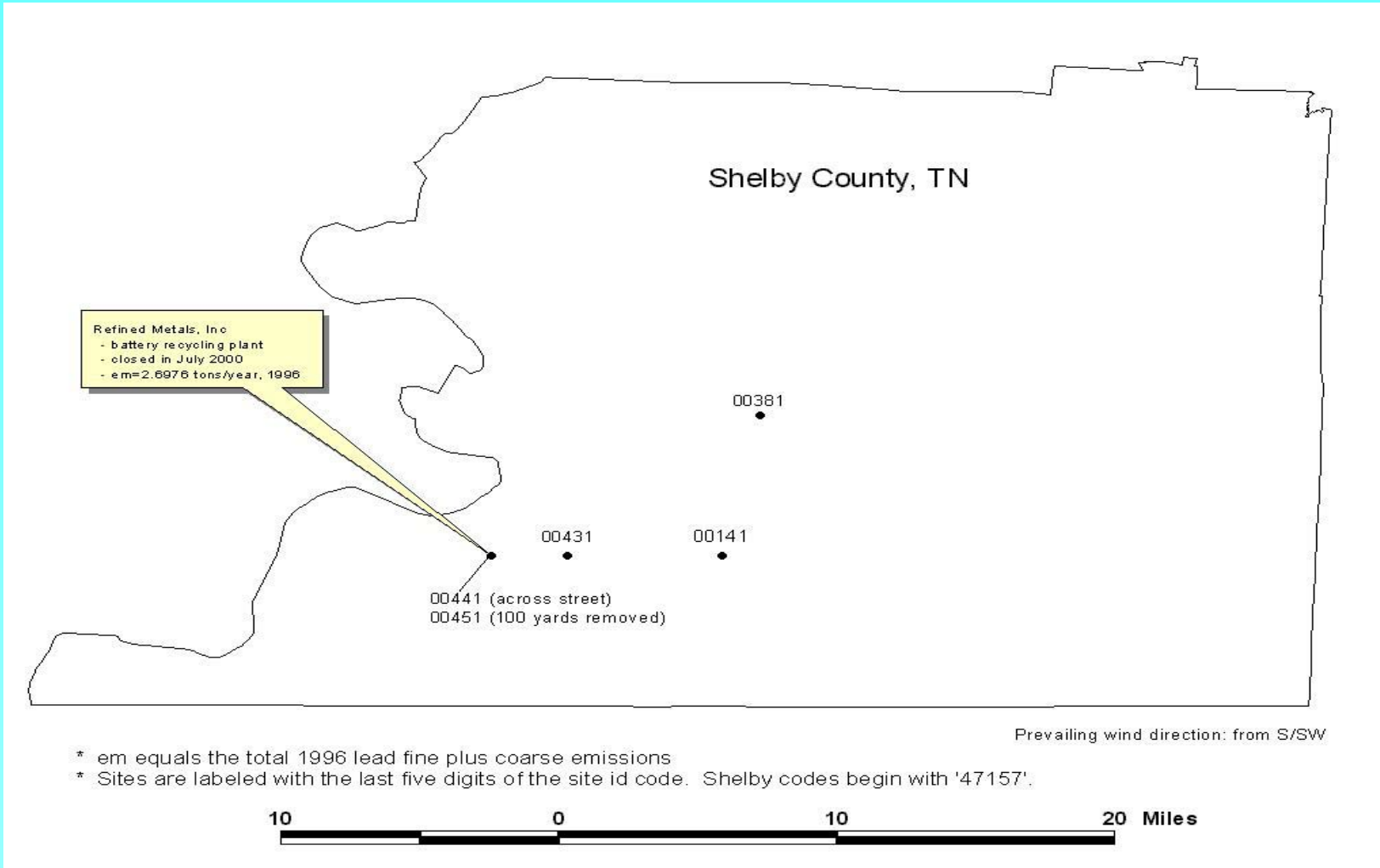
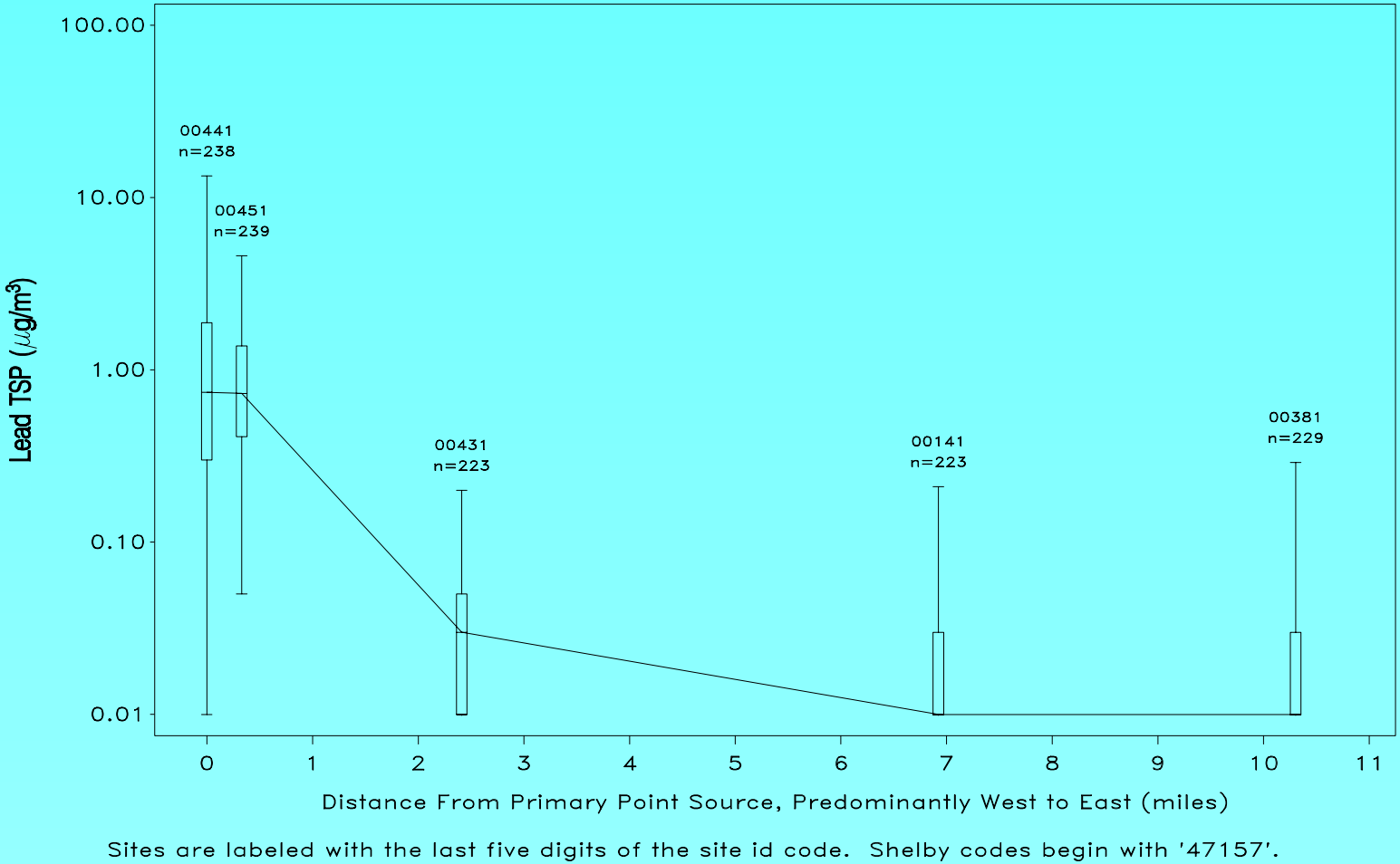
Case Study 3: Shelby County, Tennessee

- **Goal**: *Demonstrate the impact of a local point source on spatial variability and the geographic extent of the impact.*
- Five sites; 1994 to 1997
- George King of Memphis and Shelby County Health Department's Air Monitoring Division informed:
  - Two monitors within 1/2 mile of battery recycling plan
- Spatial and overall variability dropped off dramatically when source-oriented sites not included in analyses
- Impact of plant's emissions become negligible beyond about seven miles



Map of lead (tsp) monitoring sites and point source in Shelby County, Tennessee



Distribution of lead (tsp) by monitor and associated distance from primary point source in Shelby County, Tennessee

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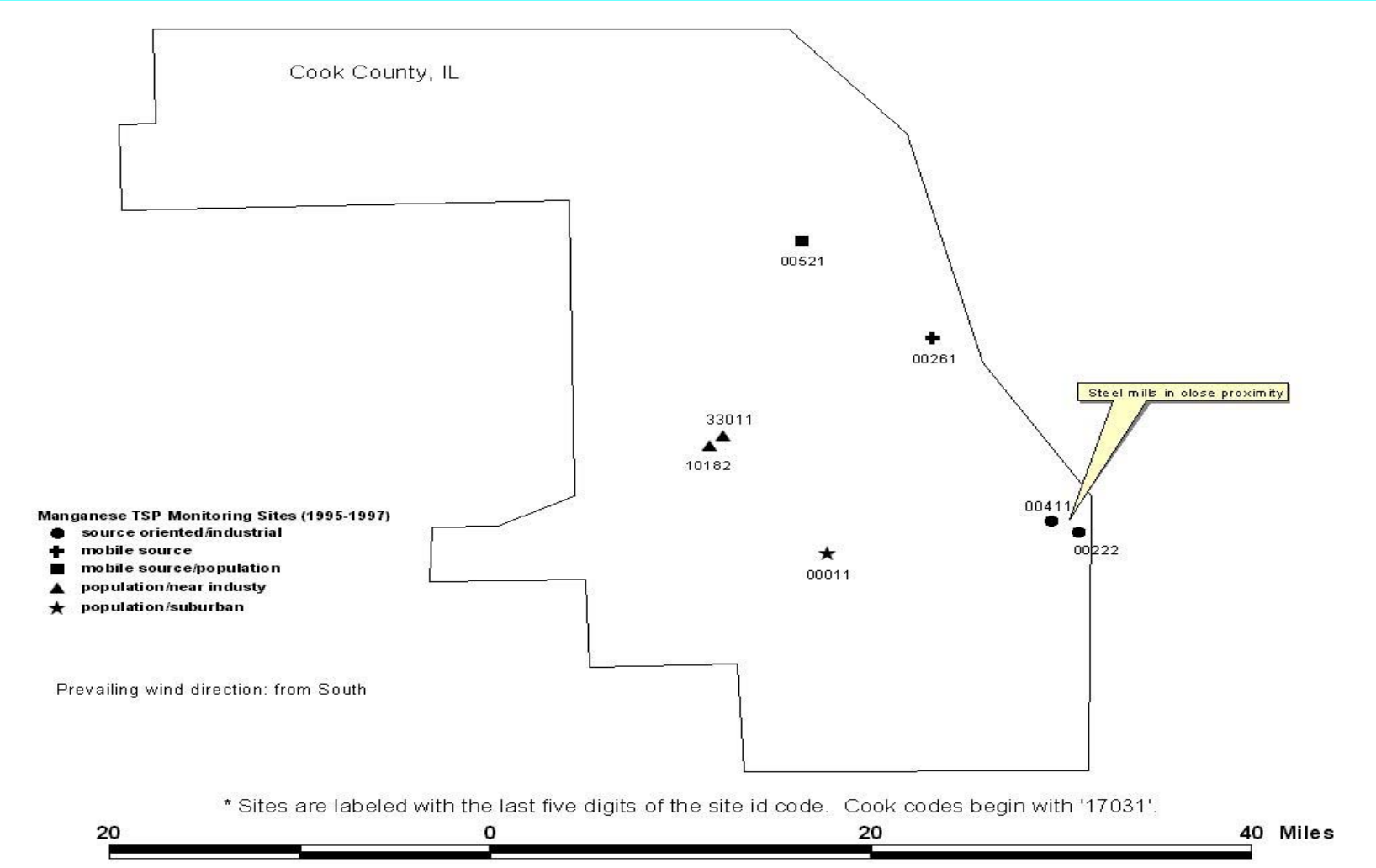
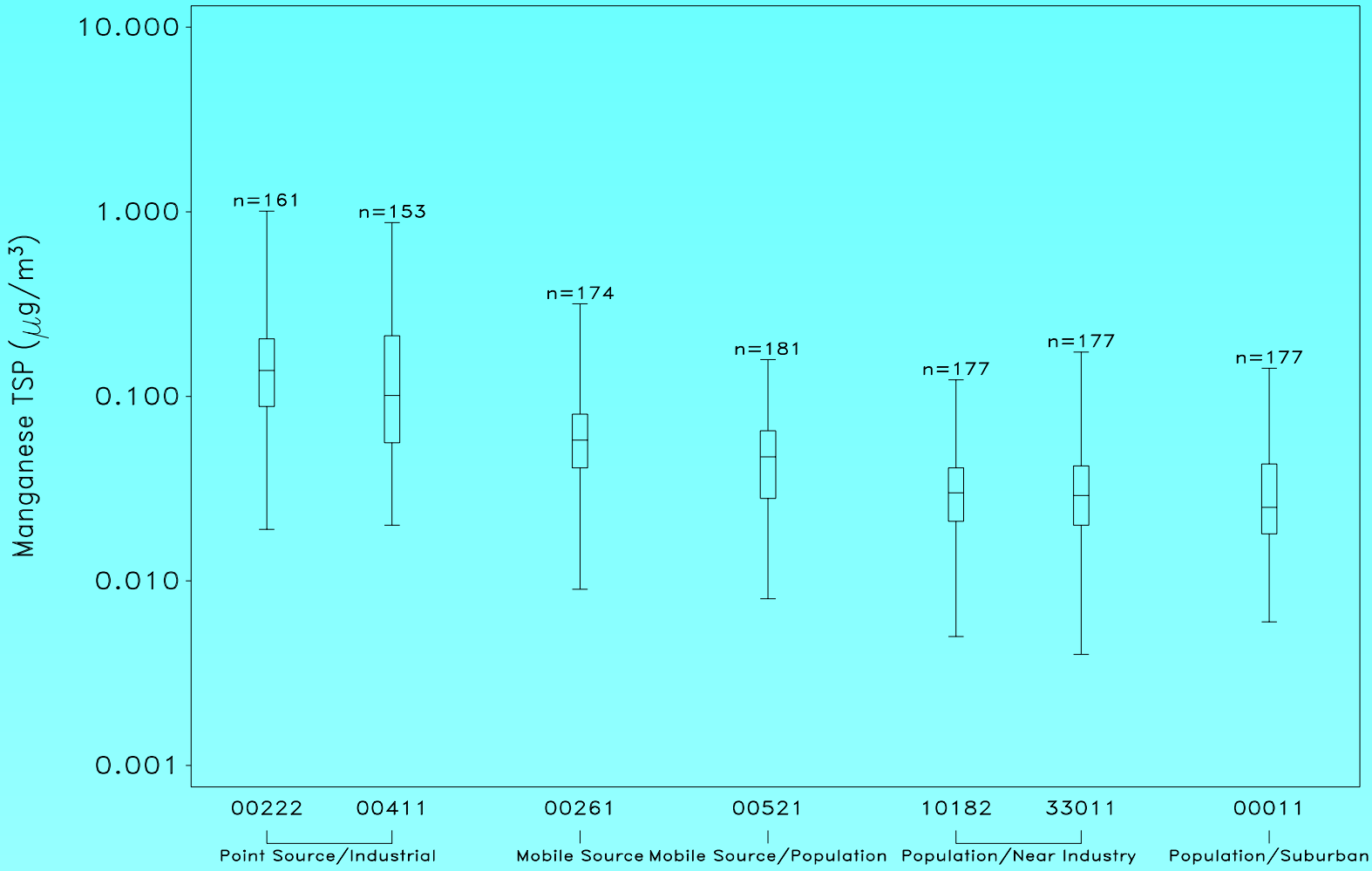
Case Study 4: Cook County, Illinois

- **Goal**: *Demonstrate the impact of local point sources and corresponding monitoring objectives on observed spatial variability.*
- Seven sites; 1995-1997
- Bob Swinford of Illinois EPA informed:
  - Two monitors in close proximity to steel mills
- Significant reduction in spatial and overall variability when source sites excluded
- Closely clustered sites tend to exhibit similar distributions



Map of manganese (tsp) monitoring sites and point source in Cook County, Illinois



Distribution of manganese (tsp) by type of monitoring site in Cook County, Illinois

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Air Toxics Pilot Study Data Analysis

Pilot City Monitoring Project

- One of two major projects as part of the first year of national air toxics monitoring
  - Pilot monitoring programs in four urban cities and six small city/rural areas
  - Sample at least 18 “core” carbonyls, VOCs, and metals
- Intended to generate information on the spatial and temporal variability of ambient air toxics concentrations.

Status of Pilot City Data

- Battelle currently acquiring all data collected at each of 10 pilot cities
  - Ambient measurements: carbonyls (TO-11A), VOCs (TO-14A/15), metals (IO-3/IO-3.5)
  - Meteorological data (temp,WS,WD,RH,sigma)
  - Other meta-information (e.g., site objective, etc.)
- Data eventually uploaded to AIRS (STI, VOCdat)
- To date, received first batch of data from ERG, and some data directly from pilot cities.

Status of Pilot City Data (cont'd.)

- Performing QA/QC and converting to appropriate SAS data sets for data analysis.

- Expect a generally complete database by early summer 2002.

Examples of Data Issues Encountered

- Numerous data formats
  - Due to time constraints, unable to wait to acquire data from AIRS.
- Apparently numerous conventions for reporting data below MDL
  - LDL and RL also used
- Numerous reporting units
  - Uncertain conversions, information missing

Upcoming Data Analyses (Examples)

- Inter-laboratory variability
  - Compare “split” samples (duplicates, replicates, multiple labs)
- MDL and reporting
  - Establish procedures for estimating “quantified” concentrations below traditional reporting thresholds.
- Monitoring data variability
  - Sources of, spatial (within-city, between-city), temporal (between-sites, seasonality), sampling and analysis uncertainty

Data Analysis Results

- Draft report planned for early 2003.
- Presentation of results at national air toxics workshop in spring 2003.